COMBUSTION PROPERTIES OF ILLINOIS COAL-CHAR BLENDS

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INTRODUCTION AND BACKGROUND

The principal product (about 60-70 percent by weight) of mild gasification (MG) processes is a partially devolatilized coal (hercin referred to as char) that must be effectively utilized to help the overall economics of the process. The loss of volatile matter (VM) indicates loss of hydrocarbon materials from the coal that are desirable for ignition, carbon burn-out and flame stability. In addition, the chars produced from processing high-sulfur Illinois coals still contain a high residual sulfur content which, when burned directly, would exceed the years 1995 and 2000 emissions limits of 2.5 and 1.2 lbs SO_2/MMBtu.

Recent research suggests that MG of a high-sulfur Illinois coal followed by a low temperature oxidation step may produce a low-sulfur char with considerable VM [1-3]. One potential use of a low sulfur-char is as a compliance fuel burned in a boiler designed to burn low-volatile fuels. The char could also be burned in conventional pulverized coal (PC) boilers with or without an auxiliary fuel such as methane or by blending with high-sulfur Illinois coal or low-sulfur Western coal. However, the combustion characteristics of low-sulfur chars have not been researched extensively. Previous results obtained at the Illinois State Geological Survey (ISGS) indicate that the char derived under MG conditions, when mixed with coal to make a 25% VM blend, can be burned with an acceptable combustion efficiency in PC boilers [3]. This paper describes our efforts to prepare a low-sulfur char from Illinois coal, blend this char with the parent coal, and determine the combustion properties of the char and coal-char blends.

EXPERIMENTAL

The chars used in this work were prepared in a continuous-feed rotary tube kiln (RTK) from an Illinois No. 2 hvCb coal, sample IBC-102 of the Illinois Basin Coal Sample Program [4]. Details of experimental methods are given elsewhere [5]. Preoxidation of -48 mesh coal was done at 150°C for 30 min in air using a feed rate of about 0.9 kg/h. The preoxidized coal was fed at 0.5 kg/h and pyrolyzed in N_2 at 600°C for 30 min. Low temperature oxidation (LTO) was done to remove sulfur from the char. Char was fed at 0.4 kg/h and oxidized at 430°C for 10 min in 17% O_2, balance N_2 during LTO.

The feasibility of decreasing SO_2 emissions during combustion tests by blending calcium-based sorbents with coal prior to charring was investigated. The coal was blended with either an ISGS high-surface area hydrated lime (HSAHL) [6, 7] or a commercially available hydrated lime (COMHYD). Coal-hydrated lime blends were prepared with 68% coal and 32% hydrated lime by weight. A continuous feed charring oven (CFCO) was used for char production [5]. The coal-hydrated lime blends were pyrolyzed in the CFCO using a feed rate of about 2 kg/h, a bed depth of 15 mm, a maximum temperature of 600°C and a residence time of about 16 min.

Five different blends were prepared from the available samples. All samples were ground to 70% -200 mesh prior to blending. The samples prepared were: 1) RTK blend - 62% (by weight) coal + 38% of the RTK char; 2) RTK_{HSAHL} blend - 92% RTK blend + 8% HSAHL; 3) $CFCO_{HSAHL}$ blend - 75% coal + 25% CFCO char (prepared from a coal/HSAHL mix); 4) $CFCO_{COMHYD}$ blend - 75% coal + 25% CFCO char (prepared from a coal/COMHYD mix); 5) $Coal_{HSAHL}$ blend - 90% coal + 10% HSAHL.

Combustion tests were done at the U.S. EPA in their Innovative Furnace Reactor (IFR) by maintaining a constant flow rate of primary, secondary and tertiary air and adjusting the fuel feed rate to achieve a constant oxygen level of about 8.0% in the effluent. This fuel feed rate corresponded to a firing rate of about 39,000 to 42,000 Btu/h. Sorbent was added downstream at a constant injection temperature of about 1200°C and at Ca/S molar ratios between 0 and about 2.4.

Selected samples were tested at the University of North Dakota Energy and Environmental Research Center (UNDEERC) in an optical access drop-tube furnace (DTF) to determine deposit growth factors, deposit strengths, and deposit compositions. Initial slagging temperatures were determined using the test conditions described elsewhere [5]. Coal was combusted at 50% excess air using a feed rate corresponding to about 0.007 g/min of ash, until a deposit of 0.6-1.0 cm had grown on the probe. The temperature was increased at 5°C/min until the deposit began to slump and consolidate (initial slagging temperature). Deposit growth factors are the ratio of deposit weight to the weight of ash fed. Fouling tests were done using conditions that simulate the environment in a boiler convective pass. Feed rates and excess air were the same as for slagging conditions. Deposit crushing strengths were determined by measuring the pressure required to crush the main portion of each deposit following removal from the DTF.

RESULTS AND DISCUSSION

Analyses of the -48 mesh samples prepared from IBC-102 in the RTK are shown in Table 1. The only significant difference between the raw coal and the preoxidized coal appears to be the slightly lower hydrogen and higher oxygen content of the preoxidized sample. During preoxidation, two processes occur concurrently, that is the gain of oxygen, and removal of hydrogen, carbon and oxygen from the coal as CO, CO_2 and water. The latter process becomes of increasing importance as the temperature is increased [8].

Table 1. Analyses of samples prepared in the RTK and CFCO (moisture free).

	IBC-102	Preoxidized IBC-102	MG char	RTK char	CFCO $Char_{HSAHL}$	CFCO $Char_{COMHYD}$
Moisture	10.96	1.57	0.79	3.42	0.73	0.74
Proximate						
Volatile Matter	40.43	39.47	15.53	19.93	32.29	33.58
Fixed Carbon	53.38	54.39	75.39	69.86	27.18	27.13
H-T Ash	6.19	6.14	9.08	9.49	40.53	39.29
Ultimate						
Carbon	74.42	74.38	80.97	77.77	45.23	46.74
Hydrogen	4.81	3.73	0.99	0.92	2.74	3.37
Nitrogen	1.38	1.33	1.76	1.85	0.97	0.99
Oxygen	9.31	9.57	3.43	7.07	8.46	7.39
Sulfate Sulfur	0.56	0.51	0.07	0.14	---	---
Pyritic Sulfur	1.45	1.48	0.18	0.17	---	---
Organic Sulfur	1.31	1.29	1.85	1.17	---	---
Total Sulfur	3.32	3.28	2.11	1.48	2.08	2.22
Btu/lb	13,330	13,225	13,284	12,499	7,271	7,830
lb SO_2/MMBtu	4.98	4.96	3.18	2.37	5.72	5.67

The pyritic sulfur content decreases and the organic sulfur content increases during devolatilization of the preoxidized coal (Table 1). Typically, 30-60% of the organic sulfur is released at pyrolysis temperatures below about 550°C [2, 9, 10]. However, Huang and Pulsifer [11] found that during pyrolysis in the presence of the gases derived from coal, only 25-33% of the organic sulfur is removed. Conditions in the RTK would be similar to those of Huang and Pulsifer because the nitrogen sweep gas flowed counter current to both to the gases released from the coal and the solid sample as it moved through the reactor. It has also been found that a significant amount of the sulfur released during pyrite decomposition can be retained in the char or react with the organic portion of the coal to form carbon-sulfur bonds [2, 11, 12].

After LTO, the VM content of the char is higher than that of the precursor char due to the chemisorption of oxygen, which is also shown by the increase in oxygen content (Table 1). These stable carbon-oxygen complexes evolve at a higher temperature than the inherent VM, and would not be expected to contribute to the flammability characteristics of the chars. The pyritic sulfur content remains constant while the organic sulfur content decreases substantially compared to the precursor char. This is unexpected, as previous researchers have found that LTO removes mainly pyritic sulfur [2, 11, 13]. The decrease in organic sulfur content may be due to the removal of sulfidic and/or elemental sulfur, which is included in the organic sulfur fraction during determination of the forms of sulfur in the char.

The SO_2 emissions of the RTK char are significantly higher than for a similar char prepared in a fluidized bed reactor (FBR) [5]. Smaller particle diameters and better gas-solid contact in the FBR may help explain this trend [5]. In addition, because the gases flowed countercurrent to the solid flow in the RTK, the SO_2 produced during oxidation may have accumulated to the point where the back reaction of SO_2 with Fe and/or the carbonaceous matrix would be thermodynamically favorable. Based on estimates of the SO_2 concentrations in the RTK during LTO, the major iron-containing product of this system would be $Fe_2(SO_4)_3$ not Fe_2O_3. This would result in lower sulfur removal than in the FBR, where the SO_2 produced is rapidly removed from the system by the fluidizing gas. A recent study found that while using a multi-step process involving oxidation, about 57% and 87% of the sulfur was removed from an Illinois coal in a fixed-bed and a fluidized-bed reactor, respectively [1].

The results of analyses of the chars prepared in the CFCO are shown in Table 1. The samples prepared with the two different hydrated limes are almost identical according to these results. The VM content of the samples includes the decomposition of $Ca(OH)_2$ and $CaCO_3$ that were present from the hydrated lime. Methods were developed to discern the portion of VM due to decomposition of calcium compounds and that due to VM remaining from the coal [5]. Overall, the VM content of the chars derived from the original coal fraction is estimated to be about 13% and 14.5% for the HSAHL and COMHYD chars. The HSAHL and COMHYD chars contained 29.9% and 29.4% CaO. Assuming that all of the sulfur released during pyrolysis was captured by the Ca-based sorbent, the amount of free calcium available in the char/lime blends for sulfur capture during combustion was 17.7% by weight.

Analyses of the coal-char blends prepared are shown in Table 2. The four samples that have Ca-based sorbents added exhibit higher ash contents, as expected. It is unclear why the total sulfur contents of these samples are also higher, but could be due to the formation of either $CaSO_4$ or CaS and their subsequent decomposition during tests to determine total sulfur contents.

Table 2. Analyses of coal-char blend samples prepared from IBC-102 (moisture free).

	RTK blend	RTK_{HSAHL} blend	$CFCO_{HSAHL}$ blend	$CFCO_{COMHYD}$ blend	$Coal_{HSAHL}$ blend
Moisture	8.95	7.78	10.21	10.61	12.62
Proximate					
Volatile Matter	31.31	33.05	39.28	38.14	40.12
Fixed Carbon	60.80	48.15	39.31	40.63	38.70
H-T Ash	7.89	18.80	21.41	21.23	21.17
Ultimate					
Carbon	76.12	70.25	65.80	66.15	65.16
Hydrogen	4.11	3.91	4.49	4.63	6.59
Nitrogen	1.49	1.39	1.27	1.25	1.20
Oxygen	7.81	3.32	4.01	3.77	2.83
Sulfur	2.59	2.33	3.02	2.96	3.05
Btu/lb	12,894	11,800	11,480	11,647	11,799
lb SO_2/MMBtu	4.02	3.95	5.26	5.08	5.17

Combustion Tests

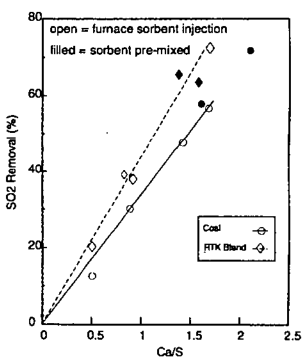

Figure 1. SO_2 removal efficiencies during IFR tests.

The SO_2 removal efficiencies for various Ca/S ratios during combustion of coal and RTK blend samples tested in the IFR are shown in Figure 1. The sorbent (HSAHL) was either physically pre-mixed with the samples or injected about 104 cm downstream (furnace sorbent injection (FSI)) of the fuel injection point. Surprisingly, the method of incorporating sorbent into the furnace does not determine SO_2 removal efficiencies. Similar results were obtained for other fuel and fuel/HSAHL mixtures, but are not shown to allow clarity. Typically, lower temperatures are used during FSI to minimize sintering of the sorbent which would decrease calcium utilization and SO_2 removal. The gas temperature at the FSI point was estimated to be about 1200°C. The temperature at the point of fuel injection was not measured during these tests. However, previous suction pyrometry data 41 cm from the burner tip for tests conducted on a Pittsburgh No. 8 coal at about the same firing rate as the present study indicated a temperature of 1250-1350°C. This suggests that the temperature difference between the two HSAHL injection points is not significant enough to affect SO_2 removal efficiencies.

The SO_2 removal efficiencies for Ca/S of 1.5 were about 52% and 66% for the coal and RTK blend fuels. The result for coal is comparable to the 50% SO_2 removal obtained with FSI of HSAHL in utility boiler tests [6, 7]. Figure 2 shows the general trend for all the samples tested in the IFR. The SO_2 removal efficiencies are greater for fuels which contain char blended with the coal. All types of chars tested enhanced the efficiency of SO_2 removal during tests. It is hypothesized that the presence of char moderates flame temperature, decreasing sintering of the sorbent, which leads to increased sorbent utilization. Ash samples collected downstream during tests using the RTK blend with and without injection of HSAHL contained about 10.8 and 5.5% carbon, respectively. It is difficult to explain the amount of residual carbon in the ash. The calculated residence time of the fuel in the heated zone (>900°C) was about 3.6 seconds with an oxygen concentration of at least 8%. Previous studies by the authors have shown that a char comparable to the RTK char achieved >90% carbon conversion at 1300°C in 6% oxygen for a residence time of 0.8 seconds [3]. The possibility that increased SO_2 removal for coal/char blends was due to incomplete char combustion was accounted for by assuming that the amount of sulfur released from the fuel corresponds directly to the amount of carbon consumed, and calculating the feed rate of fuel based on exhaust gas concentrations. The calculated feed rate was used to determine a predicted concentration of SO_2 in the gas based on analyses of the fuel. The SO_2 removal efficiency was then obtained as the difference between predicted and measured gas concentrations.

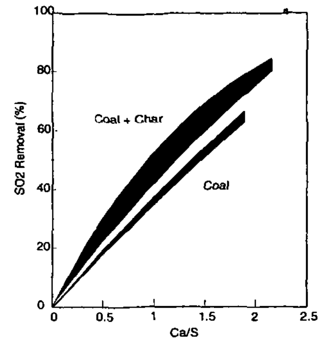

Figure 2. SO_2 removal efficiencies during IFR tests.

Figure 3 shows the emissions produced by combustion of selected fuels in the IFR. The coal produces about 4.4 lbs SO_2/MMBtu with no sorbent added. This is close to that predicted from fuel analyses (Table 1). The $CFCO_{HSAHL}$ and $CFCO_{COMHYD}$ (not shown) blends exhibit emissions similar to that for the parent coal. Due to the presence of sorbent during char preparation, the sulfur released from the coal is retained as CaS and concentrated in a smaller sample (by weight). The total sulfur content of fuels is determined at 1400°C in 100% oxygen, which decomposes the $CaS/CaSO_4$ present, allowing the entire amount of sulfur in the sample to be determined. However, in the IFR, the lower temperature (1200°C) and much shorter residence time mean that the decomposition of $CaSO_4$ is much less significant, and that sulfur present as $CaS/CaSO_4$ is not released. Since SO_2 removal efficiencies are based on total sulfur measurements, the calculated SO_2 removal efficiencies for the CFCO blends are higher than for coal (Figure 2), but because of the increased sulfur content of the blends, the overall emissions are similar.

The RTK blend and coal exhibit emissions of about 1.3 and 2.1 lbs SO_2/MMBtu at a Ca/S of 1.5 (Figure 3). This is true whether FSI is used or the sorbent is physically mixed with the samples prior to combustion. A series of tests was also done by replacing 10% of the higher heating value of the RTK blend with methane. Surprisingly, although the Btu value attributed to the methane would not be expected to have any sulfur associated with it, the RTK blend exhibits the same emissions with or without methane. The results in Figure 3 suggest that under the conditions present in the IFR, the best method of those studied to reduce the emissions of high-sulfur coals to year 2000 levels of 1.2 lbs SO_2/MMBtu would be to blend the coal with a low-sulfur char, then mix a calcium-based sorbent with the blend at a Ca/S of about 1.5.

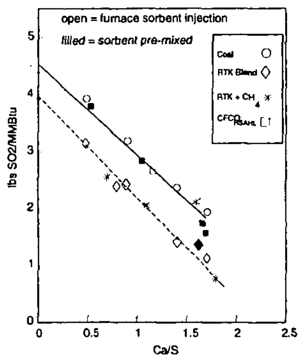

Figure 3. Emissions of fuels in IFR.

Samples tested at UNDEERC for ash deposition characteristics were IBC-102 (coal), the RTK blend and the $CFCO_{HSAHL}$ blend. The initial slagging temperatures (IST) were 1255°C for the coal, 1275°C for the RTK blend, and 1220°C for the $CFCO_{HSAHL}$ blend. The increase in IST for the RTK blend reflects the increased amount of silicon-rich species found in the deposit by scanning electron microscopy point count (SEMPC) analysis [14]. The high calcium content of the $CFCO_{HSAHL}$ blend accounts for its low IST. The deposit morphology also shows the $CFCO_{HSAHL}$ blend slagging deposit to be sintered into a nearly amorphous mass, as compared with the coal and RTK blend deposits in which individual ash particles are discernable.

Deposit growth factors for the coal and char blends were determined under both fouling and slagging conditions. Under slagging conditions, growth factors were 0.53, 0.61 and 0.64 for the coal, $CFCO_{HSAHL}$ blend and RTK blend. Under fouling conditions, growth factors were 0.46, 0.53 and 0.61 for the coal, $CFCO_{HSAHL}$ blend and RTK blend. Both blends form deposits more rapidly than the parent coal. Crush strengths of fouling deposits were 10, 29, and 0.2 psi for the coal, $CFCO_{HSAHL}$ blend and RTK blend, respectively. The high calcium content of the $CFCO_{HSAHL}$ blend, which formed a well sintered, dense deposit, accounts for its high crush strength. The RTK blend ash deposit, with more silicon-rich species and higher IST, is less consolidated than either the $CFCO_{HSAHL}$ blend or coal deposits. Although the RTK blend had the highest growth factor, the fouling deposit had a very low crush strength, indicating that it should be easily removed by soot-blowing. Conversely, the $CFCO_{HSAHL}$ blend fouling deposit had a crush strength three times that of the parent coal, indicating that the deposits will be quite consolidated and probably difficult to remove.

Behavior of the three fuels and their resultant deposits was predicted based on chemical composition data. Viscosities of the liquid phases expected to be present in each fouling deposit at 1200°C were calculated from the SEMPC results. The $CFCO_{HSAHL}$ blend deposit contained the greatest proportion of low-viscosity material, indicating a greater tendency to flow at 1200°C. The coal deposit and the RTK blend deposit had similar viscosity distributions, with less low-viscosity material than the $CFCO_{HSAHL}$ blend deposit sample. Thermal chemical equilibrium computational code that is utilized at UNDEERC to predict mineral phases and viscosities based on bulk composition data, was run for the coal and blends. The $CFCO_{HSAHL}$ blend ash exhibited a significantly lower viscosity at lower temperatures than the coal and RTK blend ashes, which are higher and nearly identical in viscosity. However, the predicted weight percentage of liquid phases in the $CFCO_{HSAHL}$ blend ash was very low at these lower temperatures, much lower than that of the coal and

RTK blend ashes. This presented two competing effects: higher-viscosity material present in significant amounts and low-viscosity material present in small amounts. However, the very-low-viscosity material present, coupled with the high ash content of the $CFCO_{HSAHL}$ blend ash, indicated that the deposition behavior would be significantly more severe than for the other two ashes.

Coal composition data were entered into an in-house EERC program that produces a fouling and slagging index. The chars were not evaluated with the program. The coal showed a potential for significant slag formation in the radiant section of a conventional PC boiler similar to that for other Illinois Basin coals. The magnitude of the index (85) is such that it may be controllable using standard remediation techniques, such as wall blowers. Severe slagging coals usually have values of 100-200. One of the main causes for the slagging potential of the ISGS coal is the high pyrite content. However, the potential for slag formation is not as high as it could be. In order to form a good low-viscosity slag, the iron from pyrite requires significant quantities of aluminosilicate clay material present, but the clay content of the IBC-102 coal is fairly low. The potential for high-temperature fouling, such as in the secondary superheater and reheater regions of the convective pass, and low-temperature fouling, such as in the economizer, should be low to nonexistent.

CONCLUSIONS

Based on results presented for the fuels in this study, the RTK blend would be the most attractive boiler feedstock because of its lower slagging and fouling potential and lower sulfur content. The best method to reduce emissions of high-sulfur coals appears to be to blend the coal with a low-sulfur char, then mix a calcium-based sorbent with the coal-char blend prior to combustion. Further studies are necessary to determine if the observed reduction in emissions by physically mixing sorbent prior to combustion is real, or an artifact of the experimental system. The results of that study would have direct implications whether to blend high-volatile, high-sulfur coals with lower-volatile, low-sulfur coals to reduce SO_2 emissions.

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REACTIVITY OF COLOMBIAN COALS TOWARD COMBUSTION

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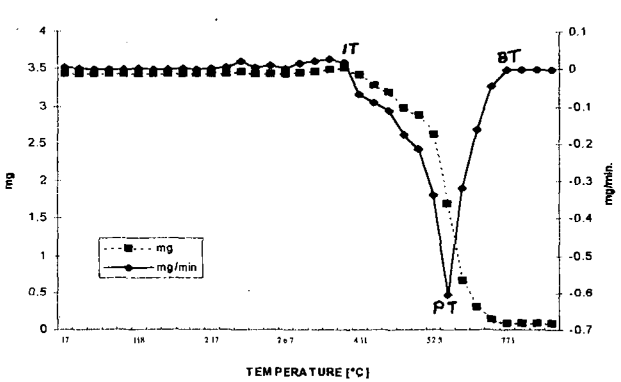
With the new world wide environment regulations, special attention is given to combustion efficiency in the electric utilities. Colombian coals are of cretaceous origen and the behavior towards combustion is different to the European and North American coals. The increase of international coal market has also created new power station operational problems in the areas of ignition, ash properties and residual carbon in ash (1) so the charaterization of coal toward combustion behavior is increasily important.. The study of pulverized coal char reactivity has been done by Drop tube reactor and Wire mesh tests. However these equipments are not common in most laboratories and easier methods must been suitable. Cumming (2) has done burning profile test to assessing the coal reactivity by DTG output from thermobalance system.. This combustion profile test has been subsecuently used by different authors (3)(4)(5)(6) as a method for characterization of coal burning properties. Pisupati (5) has found a good correlation between the Drop tube reactor test and the ignition temperature. Zhan (7) has also found that the reactivity estimated from the burn out measurement on stainless steel plate at 800°C and DTG technique in the higher temperature range match quite well.

The Martin del Corral Power Station localized near to Bogotá, is burning medium to low volatile coal and the fly ash carbon content is surprisingly high between 18-30%. The objective of the present work is to evaluted the reactivty profile of the coals used in the utility and to compare with the industrial test done in a boiler.

Experimental

Fresh samples of coals localized in the zone of influence of the Power Station were characterized and evaluated its combustibility by the combustion profile method using TGA non isotherm method.The differential thermogravimetric (DTG) test were carried out using a Perkin Elmer TGA equipment. About 5mg of pulverized sample, less than 75µm was spread into the crucible and the system was heated at a heating rate of 20 °C min^{-1} until 900 °C. A residence time at 120 °C for 5 minutes was fixed to permit the release of moisture. In the burnig profile, figure 1, three points can be clearly define; the initial temperature (IT) is defined as the temperature at which the rate of weigt loss excess 0.1% after the moisture peak., the peak temperature (TP) is defined as the temperature at which the rate of weight loss was a maximun and the burnout temperature (BP) is the temperature at which the rate loss decreased less than 1.0% min^{-1}.

FIGURE 1. COMBUSTION PROFILE



At the thermoelectric plant three coals were fired during the test in a 343.000 lb steam/h boiler. A tipical blend of the medium volatile bituminous coals a single low volatile bituminous coal and a single high volatile bituminous coal.

Results and discussion.

Table 1 shows the analytical data of the coal used. The rank of coal goes from low volatile to high volatiles bituminous C. Figure 1 shows a tipical burning profile of the coal used. The region of weight gains between 200-300°C indicates chemisorption of oxygen. Some peaks and shoulders observed before TP are believed to be due to quick release of volatile matter or to the evolution of trapped material into the macromolecular structure of coal.

In the burning profile, IT indicates the temperature at which start the evolution of small moities of organic matter and can be related with the rank of the coal used. Figure 2, shows that there is an increase of the IT as the rank of coal increases. The related curve has two breaks at 80%C and 87%C which correspond to the coalification jumps of the bituminous coals. Similar tendency can be observed for PT, figure 3. Not correlation was found for the BP. It is well known that the volatile matter content [VMC] is an indicative of the rank of coal and as expected a good linear relation with a 0.83 correlation factor, was found for the IT, as shown in the figure 4. The lower IT (297.10 °C) was found for the higest VMC (46.39%) while a IT of 348 °C was found for the lowest one (20.23%).

FIGURE 2. IT VS % C

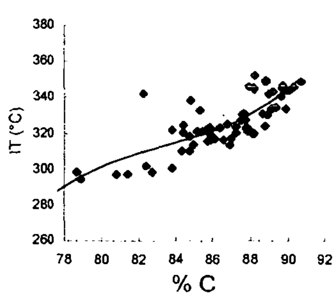
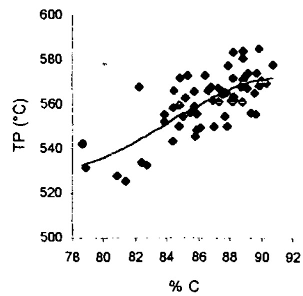


FIGURE 3. TP vs % C



Pisupati (5) has found a good correlation betwen IT and the combustion efficience in an industrial scale demostration boiler. In this work a good correlation was found between IT and the VMC, indicating that it is a good index for study the behavior of coal during combustion and this criteria was used for the selection of the industrial test. Table 2 shows the analytical data of the coal used in the industrial scale test. The boiler efficience the three coals were: 80.89 for the coal with the lower VMC; 84.74 for the coal with the highest VMC and 83.70 for the industrial blend.

FIGURE 4. IT vs % MV

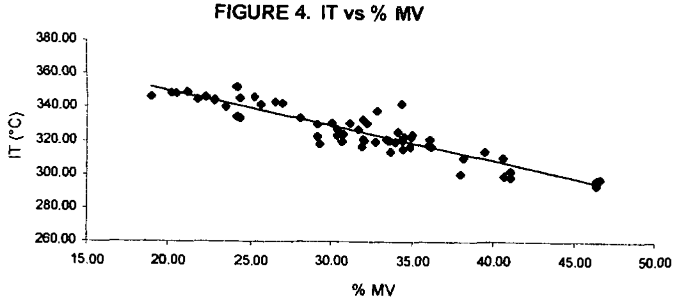


Table 1. Analytical data of the coal used.

Sample No	%H_2O (a)	%Ash (a)	%V.M (b)	%C (b)	%H (b)	%N (b)	%S (a)
1	0.89	8.05	30.35	86.39	5.49	1.83	0.81
2	1.02	10.03	30.68	87.25	5.60	2.00	0.92
3	0.85	14.12	34.14	86.79	5.63	2.25	0.89
4	1.94	6.90	32.71	88.21	5.71	2.04	1.17
5	1.22	4.55	22.77	89.65	5.00	1.78	0.58
6	0.97	12.82	25.60	89.02	5.31	1.96	0.45
7	1.40	14.48	21.81	88.21	4.97	1.64	0.35
8	1.40	5.15	22.38	89.71	4.62	1.77	0.51
9	0.95	3.64	23.50	89.56	5.08	1.80	0.69
10	0.90	20.51	33.55	84.43	5.92	1.79	0.88
11	1.04	22.61	34.33	82.28	5.53	1.96	7.15
12	1.10	25.87	35.04	84.40	5.86	1.93	1.47
13	0.93	9.64	36.12	85.46	5.83	2.05	1.24
14	0.80	20.67	32.78	84.82	5.65	2.08	4.34
15	1.04	5.96	32.16	88.68	5.63	1.82	1.03
16	2.24	9.30	46.63	80.80	6.31	1.79	1.33
17	0.99	4.76	18.99	90.31	4.71	1.71	0.44
18	1.14	8.37	38.13	84.77	5.89	2.01	0.76
19	1.16	12.84	34.51	85.70	5.67	1.93	1.59
20	0.96	5.53	24.31	89.87	5.19	1.87	0.45
21	0.79	13.24	29.17	88.89	5.64	1.99	0.79
22	0.68	5.70	24.32	88.20	5.27	1.86	0.65
23	1.18	14.92	40.61	84.36	6.05	1.91	0.68
24	1.48	10.86	41.02	82.42	5.85	1.76	1.84
25	1.11	13.14	34.41	83.84	5.71	1.88	2.06
26	1.16	11.10	39.42	84.99	5.82	1.80	0.99
27	2.26	18.52	46.39	81.42	6.46	1.75	1.64
28	2.61	14.09	46.43	78.90	6.31	1.79	2.98
29	1.88	19.72	40.66	78.66	6.02	1.67	0.59
30	0.92	21.57	29.31	84.78	5.86	1.86	1.10
31	1.12	15.81	36.01	86.96	5.93	1.94	0.39
32	2.15	5.54	41.06	82.74	6.03	1.79	0.81
33	0.92	16.24	33.40	85.18	5.79	1.87	0.93
34	0.85	12.18	34.40	85.68	5.70	2.15	1.09
35	0.68	21.23	25.27	87.91	5.17	1.66	2.04
36	2.26	3.33	38.03	83.83	5.79	1.82	0.52
37	1.03	9.03	34.83	86.11	5.71	2.00	1.10
38	1.26	6.06	36.16	85.88	5.76	1.82	0.70
39	0.76	20.50	24.17	88.23	5.17	5.97	1.20
40	0.98	6.33	34.42	87.27	5.55	1.89	0.49
41	1.08	5.48	34.91	85.84	5.66	1.92	1.02
42	1.29	7.82	31.99	87.85	5.55	1.86	0.65
43	0.93	11.52	29.16	87.79	5.60	2.00	2.03
44	1.18	4.77	33.98	85.82	5.70	1.85	0.71
45	1.57	4.70	33.62	86.88	5.54	1.93	0.48
46	1.09	6.08	31.69	87.70	5.59	1.87	1.03
47	1.35	5.45	31.91	86.60	5.52	1.92	0.44
48	0.70	6.42	31.16	87.62	5.52	1.93	0.65
49	0.96	4.86	32.01	88.05	5.65	1.83	0.89
50	1.01	3.75	31.99	85.31	5.38	1.90	0.53
51	1.13	6.18	30.02	87.57	5.47	1.87	1.21
52	0.86	10.13	26.96	89.18	5.46	1.97	1.14
53	0.95	5.14	30.38	87.49	5.61	1.83	0.81
54	0.90	4.72	30.71	88.77	5.46	1.90	0.45
55	1.17	3.96	30.66	88.14	5.41	1.72	0.39
56	0.78	5.09	28.04	89.11	5.45	1.75	0.71
57	0.66	4.28	26.57	90.04	5.31	1.75	0.55
58	0.98	9.96	21.21	88.84	4.93	1.79	0.49
59	0.81	7.78	22.80	89.87	5.11	1.75	0.50
60	0.70	4.18	24.16	89.31	5.08	1.72	0.45
61	0.73	7.68	20.53	88.87	4.83	1.78	0.50
62	0.79	4.69	20.23	90.71	4.73	1.70	0.53

Where:(a), as determined; (b), moisture ash free basis

Table 2. Analytical data of the coal used in the industrial boiler test.

Sample	%H_2O (a)	%V. M (a)	%Ash (b)	%C (b)	%H (b)	%N (b)	%S (a)
003	2.04	30.03	19.38	84.63	4.20	1.65	1.48
163	1.37	26.65	16.91	87.78	4.06	1.95	0.96
mixture	1.53	27.89	20.12	85.55	4.08	1.70	1.57

Where:(a), as determined; (b), moisture ash free basis

This results shows that when working with bituminous coal the VMC is a good approach for the design of the burning coal blend. To have high volatile coal in the blend is important since its ignition temperature is lower and it will be the first ones in burning, given full speed in the burning of the other coals.

Acknowledgments

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A LABORATORY ASSESSMENT OF THE SLAGGING PROPENSITY OF BLENDED COALS

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ABSTRACT
This paper presents the results of an experimental study to assess the slagging propensity of blends of UK coals with world traded coals when burned under low NOx conditions. Coals ground to pulverised coal grade were blended in a laboratory mixer. Ash deposits were formed by passing the coals through an entrained flow reactor designed to simulate the time-temperature conditions which pulverised coal particles are subjected to in a large utility boiler. The deposits were collected on a ceramic probe at approximately 1250°C. The slagging propensity of the coal ash was assessed from a CCSEM chemical and microstructural characterisation of mounted and polished cross-sections of each deposit. The CCSEM data was used to obtain an estimate of the fraction of the deposit which would have been fluid enough for viscous flow sintering to have occurred, producing fused and bonded portions of the slags. The results indicate that the slagging propensity of a coal blend may be a non-linear function of the composition, showing both positive and negative deviations from a simple additive relationship. The findings are discussed in terms of the mineral matter transformations which occur in forming ash particles and boiler wall deposits.

INTRODUCTION

The efficient operation of modern pulverised coal-fired boilers is dependent on fuel quality, high conversion efficiencies and a high availability of plant. The nature and quantity of mineral matter in a coal can have a profound effect on the operation and performance of the boiler. Boiler slagging not only reduces the thermal efficiency of a boiler but can give rise to other problems, such as high exit gas temperatures leading to increased fouling of superheaters and economisers. The formation of large wall deposits on water walls and superheaters can lead to blocked ash hoppers and fractured boiler tubes.

Fuel technologists have long sought reliable methods for predicting the slagging propensity of a coal ash (1). Conventional methods of assessment based on ash fusion tests, viscosity of coal ash melts and empirical indices related to the chemical composition of the ash (2) all fail to reflect the complex mineral matter decompositions and reactions which occur at the combustion temperatures. In addition, the short residence times for ash particles within the burner region (1-2 sec) frequently do not allow the larger mineral particles to reach chemical equilibrium. Advanced microstructural analysis, combined with chemical analysis of individual ash particles obtained using computer controlled scanning electron microscopy (CCSEM), has demonstrated the diverse chemical nature of ash particles and the lack of chemical homogeneity (3). Thus, to obtain reliable data, fuel technologists have developed combustion test facilities which closely simulate the conditions in large pulverised coal boilers. The results obtained with these facilities still require validation with full scale boiler trials, as recently reported by Gibb et al (4). The cost of such trials, and the need to obtain objective assessments of the slagging propensity of a coal ash provided the stimulus for the design and construction of a laboratory entrained flow reactor (EFR) at Imperial College (5) to simulate ash formation and deposition phenomena.

The EFR was designed to closely simulate the conditions which pf and ash particles experience in large utility boilers. The reactor consists of a vertical multi-zoned furnace, approximately 5m in length, with an internal diameter of 100mm. Four independently controlled furnaces heat the reactor, providing a temperature gradient from 1650°C at the top of the reactor to 1200°C or less at the bottom. A series of sample ports at approximately 1m intervals down the length of the reactor allow ash and char samples to be withdrawn from the combustion atmosphere, or for deposition probes to be inserted . Pulverised coal is introduced at the top of the furnace at a rate of 50-200g hr^{-1}, the chosen feed rate largely depending on the ash content of the coal or blend under investigation. Gas flow rates of approximately 70 l min^{-1} (STP) , equivalent to 450 l min^{-1} at 1650°C entrain all particles with a density of 5 g cm^{-3} or less and a particle size of < 80μm. Under these conditions, particle residence times from top to bottom of the reactor are approximately three seconds. The reactor is shown schematically in Fig.1, with the position of the sample ports. Gas temperatures at the top sample port are approximately 1400°C and 1250°C at the second port.

Both air-cooled metal deposition probes and uncooled ceramic probes have been used to collect ash deposits. Deposits collected at 1400°C at the first port must be collected on a ceramic probe, as it has not been possible to provide sufficient cooling of a metal probe at this port to prevent the probe from melting. The deposits are generally of a highly fused nature and give little indication of the likely slagging propensity of the coal. However, when deposits are collected at 1250°C on an uncooled ceramic probe, they range from a thin covering of lightly sintered ash particles to well-bonded and coherent deposits, the nature of the deposit depending on the proportions of the mineral matter present in the coal. These deposits most closely resemble those which form on the platten superheaters of large utility boilers and are therefore suitable for characterisation.

The ceramic probe used in this study was of simple construction, consisting of a mullite tube or coupon, 16mm OD and 12.5mm ID, and 200mm in length. The coupon is held in place over a longer (approximately 1m) mullite tube of 12mm OD. The coupon is held in place with a small amount of a high alumina cement mixed with a sodium silicate solution. The same cement was used to block the open end of the 12mm tube, thus preventing gas leakage into or out of the reactor. An aluminium holder with an "O" ring seal is used to hold the probe in position in the sample port.

CHARACTERISATION OF DEPOSITS

Over a 1-2hr period, the deposits varied in thickness from 2-8mm depending on the ash content and mineral matter in the coal and the feed rate. A small sample of the deposit is first removed for X-ray powder diffraction analysis to establish the crystalline phases present, while the remainder of the deposit is left undisturbed on the coupon. The deposit is then coated in a low viscosity epoxy resin, which penetrates the open porosity of the sample, but when set gives stability to even the most fragile deposits. Sections through the deposit are cut with a diamond saw, perpendicular to the surface, to give samples approximately 5mm in length. These samples are then set in resin blocks so that a cross-section through the deposit from the interface with the probe to the surface of the deposit may be examined. The samples are ground and polished to a 0.25μm diamond finish, and coated with carbon for SEM examination. At low magnification (10x) a series of backscattered images (BSI) is first obtained to give an overall view of the microstructure of the deposit. More detailed examination is then made of selected areas at higher magnifications, typically 50-100x. Quantitative chemical and image analysis data is then acquired using a Tracor Noran low element detector and Tracor Noran Voyager software. Typically, a chemical analysis is acquired using a 16x16 matrix of analysis points, giving 256 separate analyses. Quantitative EDS analyses are obtained from this data using Proza corrections. The porosity of the microstructure, which gives a strong indication of the amount of viscous flow sintering which has occurred, may be obtained from a grey scale digital image which differentiates between the ash and the resin (i.e. the filled pores) or from the fraction of analysis points reporting oxide analyses, where the criteria used for this are that analyses with $\Sigma(CaO+Fe_2O_3+Al_2O_3+SiO_2) > 80$wt% can reasonably be assumed to be an oxide particle. The chemical and microstructural data is collected from a number of areas within each section and from samples taken at intervals along the coupon length. Typically, the number of analysis points exceeds 1000, thus giving sufficient data for reliable statistical variations to be established.

An assessment of the slagging propensity of the ash is made by a consideration of the analysis and the chemical variations shown by the ash particles and the bonding phase(s). The four main oxides which make up the ash composition are CaO, Fe_2O_3, Al_2O_3 and SiO_2, and the chemical data may be analysed by normalising each ash composition to two ternary systems, i.e. CaO-Al_2O_3-SiO_2, and Fe_2O_3-Al_2O_3-SiO_2. Only those analyses where $\Sigma(CaO+Al_2O_3+SiO_2)$ or $\Sigma(Fe_2O_3+Al_2O_3+SiO_2)$ exceeds 80 wt% are taken, since the normalisation of compositions totaling less than this could lead to substantial errors. The data obtained may then be plotted on a ternary diagram, see for example Fig.2. Each plot shows not only the range of chemical compositions obtained by analysis, and thus the degree of chemical inhomogeneity in the sample, but also indicates the degree of interaction between the decomposed mineral residues, i.e. the clays (kaolinite and illites), pyrite, calcite, quartz etc.

The quartz and decomposed clays can be considered as relatively refractory materials at the combustion temperatures. Indeed, coals which contain only these minerals give few problems with regard to boiler slagging. Any ash which forms on the boiler walls is little more than a friable dust with no mechanical strength. Slagging problems arise if the mineral matter contains additional minerals such as pyrite (FeS_2), calcite ($CaCO_3$), dolomite ($Ca.Mg(CO_3)_2$), siderite ($FeCO_3$), and ankerite ($Ca.Fe(CO_3)_2$. Each of these minerals decomposes to give the respective oxide, which acts as a strong fluxing agent for the aluminosilicate phases, lowering both the liquidus temperature and the viscosity of the melt. On a mole for mole basis, FeO is a more powerful fluxing agent than CaO, since the Fe^{2+} ion is smaller in size than the Ca^{2+} ion, enabling the aluminosilicate anions to move over each other more readily. Aluminosilicate ash particles which have been fluxed with either FeO or CaO, or both, have the potential to form sticky ash particles which will not only adhere to a surface (water wall or deposit) but will bond together the more refractory ash particles. Exactly how much FeO or CaO is required to form a sticky ash particle remains open to debate, but lower limits of 5-10 wt% would be considered a reasonable estimate. At higher concentrations of FeO or CaO, a reverse of the fluxing role of these oxides is observed. In the case of FeO, a solubility limit is reached, and the excess iron oxide is precipitated from solution in the form of iron oxide dendrites (magnetite or haematite). Ash particles with more than 50 wt% Fe_2O_3 are therefore more than likely to be mainly solid crystalline iron oxides and thus of relatively low slagging propensity. CaO, which itself is refractory oxide, lowers the liquidus temperature and the viscosity of aluminosilicates, with a maximum effect on coal ash compositions at 25-30 wt% of added CaO. Further increases lead to increasing liquidus temperatures and a reduction in the amount of liquid phase present (6). Ash particles with 40% or more of CaO may similarly be considered as non-slagging particles, at least in the early stages of the formation of deposits. An EFR slagging index has therefore been established by determining the fraction of ash particles which contain 10-50 wt% of Fe_2O_3, or 5-40 wt% CaO.

COAL BLENDS

Two UK power station coals (coals 1 and 2) were chosen for blending with a Colombian coal (coal 3), two US coals (coals 4 and 5) and a South African coal (coal 6). The ash content and ash composition for each of these coals is shown in Table 1. Coals were each ground separately to pf grade, i.e. 70% less than 75μm. The coals were then blended in a laboratory mixer in batches of 1-2 kg. Coal were dried at 110°C for several hours before feeding to the EFR for the ash deposition studies. Failure to dry the coals sufficiently resulted in uneven flow rates of pf from vibratory hopper, which in turn caused blockages of the pf in the water-cooled injection probe at the top of the reactor.

RESULTS AND DISCUSSION

The results of blending coal 1(UK) with coal 3(Colombian) are shown in Fig.3. In order to assess the sensitivity of the EFR slagging index, the CCSEM data has been analysed here using three sets of compositional limits in determining the fraction of ash particles which would be deemed to be of a fluxed nature and a low viscosity. The conditions chosen were as shown below.

Conditions	CaO (wt%)	Fe_2O_3 (wt%)
A	5-40	10-50
B	5-45	5-55
C	10-35	15-45

In all three cases, the variations in slagging propensity with the addition of coal 3 are similar, with initially an increase in slagging propensity which shows a significant positive deviation from a simple law of mixtures. Conditions B, which provide the widest compositional limits give the highest values for the EFR slagging index, while conditions C, with the narrowest range give the lowest values. Conditions C also show the smallest variations and thus the least sensitivity to compositional changes and related microstructural changes. Fig. 4 shows the variations in slagging indices obtained on blending the two UK coals with the overseas coals. In each case , major deviations were observed from a simple linear relationship between the slagging index and the blend composition. The data shown in Fig. 4 was obtained using the compositional limits A in each case. These conditions were chosen as giving the optimum measure of the compositional variations in each deposit. In each case, the addition of the overseas coal initially gave a marked increase in the slagging propensity, with a maximum value in the range 25-50 wt% of added overseas coal. Above 50 wt% of the added coal, the slagging propensity decreased, in two cases with negative deviations from a linear relationship.

In a blended pf, there are basically two types of mineral matter. Most of the adventitious mineral matter present in the original coal is liberated as discrete mineral particles during the grinding process, while the finely distributed inherent minerals remain within the coal particles. It is generally assumed that the discrete mineral particles exhibit little interaction during the ash formation processes, reacting only with other ash particles on deposition. Inherent minerals interact and coalesce during the combustion of the char and are responsible for the wide range of aluminosilicate compositions observed for ash particles. Synergistic effects between ash particles suggests that complex interactions between particles must occur, and these are most likely to take place following deposition to form the slag.

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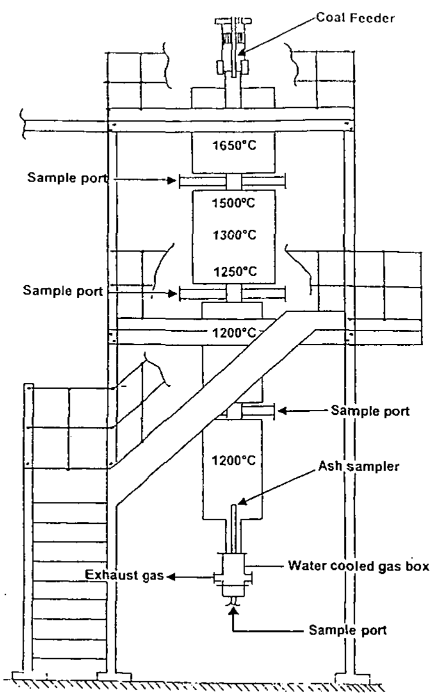
Table 1 Coal ash compositions (wt%) and ash contents

Coals	1	2	3	4	5	6
wt% ash	9.8	16.0	8.6	8.7	8.5	14.8
SiO_2	41.9	56.0	63.5	50.0	48.2	40.7
Al_2O_3	24.3	26.4	19.9	25.6	21.1	32.7
Fe_2O_3	20.9	6.5	8.5	14.6	16.5	2.4
CaO	7.1	1.9	2.6	4.5	4.4	9.3
MgO	3.3	1.7	1.7	1.0	1.0	2.5
Na_2O	0.1	1.5	0.6	0.8	1.4	0.4
K_2O	1.0	4.0	2.2	2.0	2.2	0.7
P_2O_5	0.2	0.1	0.2	0.4	0.3	1.4
TiO_2	1.0	1.0	0.9	1.2	1.2	1.7
MnO	0.2	-	0.1	<0.1	-	-



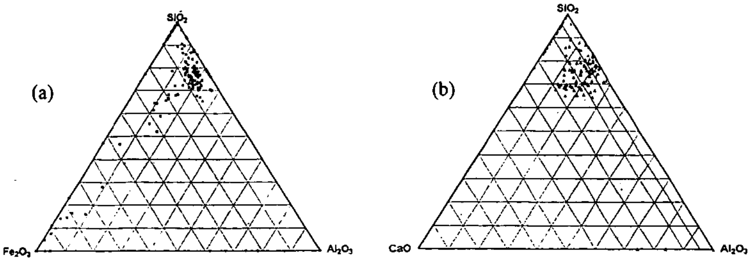


Fig. 2. Chemical inhomogeneity of slags as shown by EDS point analysis of polished cross-sections. Each composition has been normalised to (a) Fe_2O_3+Al_2O_3+SiO_2, and (b) CaO+Al_2O_3+SiO_2 for plotting. Shaded areas are compositions deemed to be slagging.

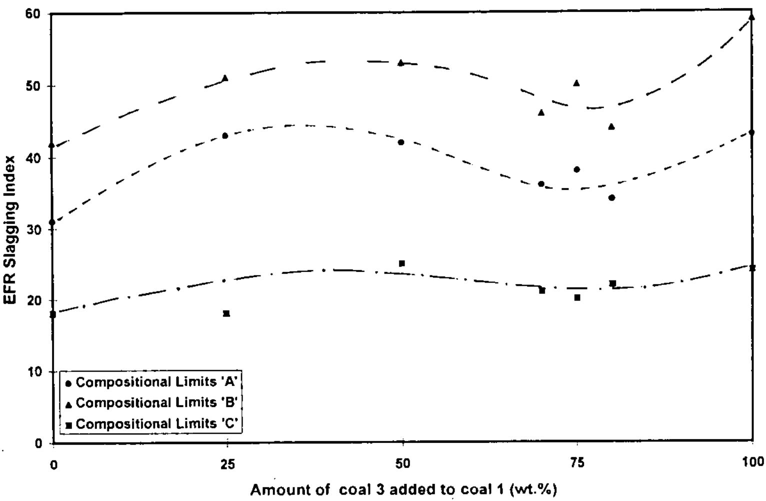


Fig. 3. Variation in EFR slagging index obtained with blends of coal 1(UK) with coal 3 (Colombian). Compositional limits A,B and C represent different concentrations of Fe_2O_3 and CaO in fluxed ash particles, see text for full details.

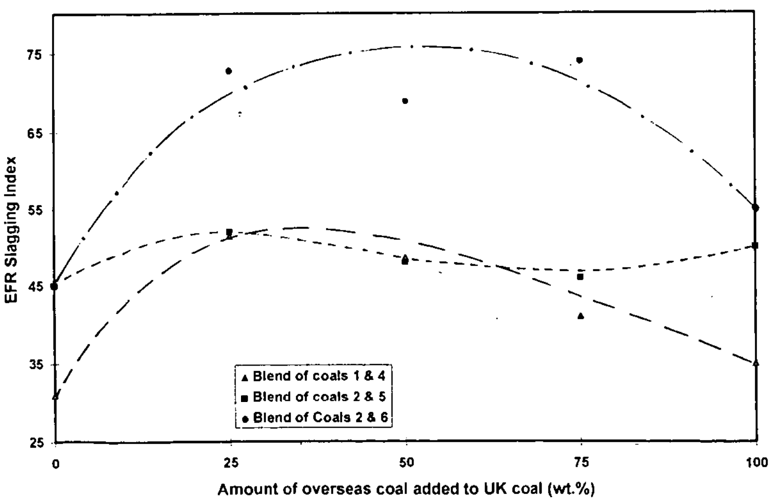


Fig. 4. EFR slagging indices for blends of UK coals 1 and 2, with overseas coals 4, 5 and 6.

CLASSIFICATION OF INDIAN COALS FOR COMBUSTION

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1. INTRODUCTION

In annual coal production India ranks fourth in the world, behind China, USA and Russia, with an estimated production of 225 million tons in 1995-96. The utilities burn nearly 60% of the mined coal while industries consume 25-30% of the coal for captive power generation and process heat. The remaining 10-15% goes for the production of coke and miscellaneous applications. Combustion is thus the most important use of coal in India or for that matter, anywhere in the world.

Countries like USA have national coal sample banks and databases. The Pennsylvania state (PENN) coal sample bank and database are well known, which are also used by the US Department of Energy(DOE). The Argonne National Laboratory has used 200 samples from the PENN coal database and using cluster analysis, has identified 8 representative samples among American coals. Similar exercises have been carried out by Illinois Coal Development Board, US DOE's Pittsburgh Energy Technology Center and several universities. The need for a similar coal data bank/database for India and the lack of it at present have been highlighted by Nandakumar and Gopalakrishnan (1988). Especially, for the design of combustion equipment, it will be highly helpful if one can come up with a set of typical Indian coals.

Classification schemes have similar objectives. However, a classification system meant exclusively for combustion applications or for Indian coals does not exist nor is it likely to be developed with the present approaches. Many classification schemes restrict themselves to two or three coal properties but the picture is not complete. If too many properties are involved, classification gets complicated and ends up as a coding scheme. In general, rank, calorific value, proximate and ultimate analyses, fuel and atomic ratios and petrography seem to be the most important variables for characterizing a coal's combustion behaviour. They are highly inter-related, as revealed in the literature. Is it possible to develop a classification system using all these properties and still achieve a reasonably simple grouping? Principal component analysis (PCA) offers a solution, under certain conditions.

2. PCA METHODOLOGY

Principal Component Analysis(PCA) consists of finding an orthogonal transformation of the original variables to a new set of uncorrelated variables, called principal components (PCs), which are derived in decreasing order of importance (Chatfield and Collins, 1980). The usual objective of the analysis is to see if the first few components account for most of the variation in the original data. If they do, then the dimensionality of the problem is reduced. With two PCs, plotting the values in a graph can reveal some patterns in the data.

To validate this proposition, a reference dataset, preferably non-Indian (to avoid biases) and fairly well structured, is needed. Hensel (1980) has used a reference table of US coals for studying combustion and classification and this table will be used for the comparisons. Leaving out lignite-B, of which there are no known reserves in USA or Canada, Hensel has selected eight to eleven coals for each of the remaining 12 groups in the ASTM ranks containing a total of 119 samples. The table contains the Calorific value (Cvd), proximate analysis (Fd and Vd) and ultimate analysis (Cd, Hd, Od, Nd, Sd) on a dmmf basis, to which F/V, C/H and CH/O will be added. Petrographic information is not available and hence is left out for the present exercise. Thus the table serves a dual purpose - it covers the entire spectrum of ranks (except lignite-B) and will serve as a good background for the Indian data. It will also help to compare the Indian and US coals.

The analysis can now be gone through in stages. First, one has to decide about the variables. Since Fd and Vd are complementary, one will do. The variables have to be standardised to have unit variance. The correlation matrix is computed next (Table-1). Of the 10 variables listed, Nd and Sd show poor correlation with the other variables. Nd and Sd are relatively outsiders and hence were left out of the analysis.

Table-1 Correlation matrix between variables

	Cvd	Fd	Cd	Hd	Nd	Sd	Od	F/V	C/H	CH/O
Cvd	1.00	0.71	0.89	−0.30	0.11	0.14	−0.95	0.30	0.40	0.71
Fd	0.71	1.00	0.93	−0.84	−0.34	−0.12	−0.85	0.74	0.84	0.93
Cd	0.89	0.93	1.00	−0.65	−0.16	−0.05	−0.97	0.63	0.73	0.90
Hd	−0.30	−0.84	−0.65	1.00	0.55	0.19	.51	−0.90	−0.96	−0.78
Nd	0.11	−0.34	−0.16	0.55	1.00	0.04	.04	−0.53	−0.53	−0.29
Sd	0.14	−0.12	−0.05	0.19	0.04	1.00	−0.13	−0.16	−0.17	−0.05
Od	−0.95	−0.85	−0.97	0.51	0.04	−0.13	1.00	−0.50	−0.60	−0.85
F/V	0.30	0.74	0.63	−0.90	−0.53	−0.16	−0.50	1.00	0.97	0.73
C/H	0.40	0.84	0.73	−0.96	−0.53	−0.17	−0.60	0.97	1.00	0.81
CH/O	0.71	0.93	0.90	−0.78	−0.29	−0.05	−0.85	0.73	0.81	1.00

The eigen values of the reduced correlation matrix are calculated (Table-2).

Table - 2 Eigen values

	1	2	3	4	5	6	7	8
value	6.26	1.41	0.17	0.09	0.03	0.02	0.01	0.00
%	78.24	17.64	2.17	1.13	0.37	0.29	0.12	0.04
cumulative%	78.24	95.88	98.06	99.19	99.56	99.84	99.96	100.00

The first two eigen values alone are significant and account for nearly 96% of the information. The eigen vectors were next worked out and used to transform the variables to principal components (PC). The PCs corresponding to the first two eigen values for all the samples were plotted in a graph (Figure-1a). **Alphabets are used as symbols and follow the rank**. Thus 'A' refers to meta-anthracite and 'L' refers to lignite-A.

This curve is comparable to the Seyler graph in the sense that with two (pseudo) properties, it enables one to compare several coals. It has in fact captured the essence of all the eight chosen coal properties. The clustering of coals of the of same rank is clearly visible in the figure as also the smooth transition from meta-anthracite at one end to the lignites at the other end. Anthracites and low volatile bituminous coals fall on one side. The high volatile coals and lignites fall on the other side. The medium volatile bituminous coals are near the peak. **This is a new discovery and has not been reported in literature so far.** The graph does not change if mean values alone are used (Figure-1b)

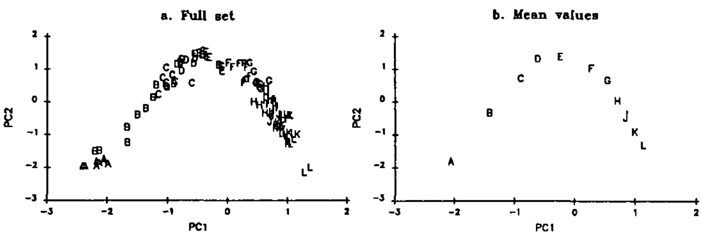

Figure - 1. Principal Components - ASTM Coals

To explore the relationship between PCs and the variables, PC1 and PC2 were plotted against the other variables. The graphs display a rank based continuity and the inescapable conclusion is that the PCs represent the rank in essence. Variation of Cv, Cd and F/V with PCs alone are shown to illustrate the point (Figure- 2 & 3).

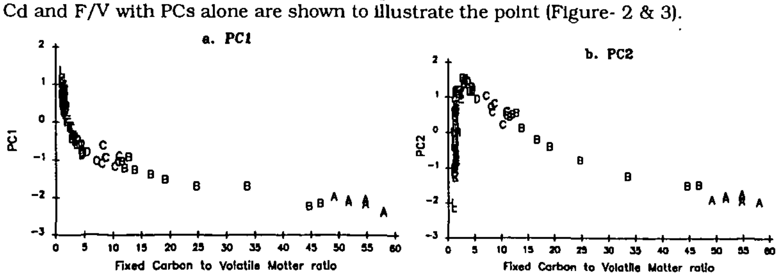

Figure - 2. Principal Components and Fuel Ratio

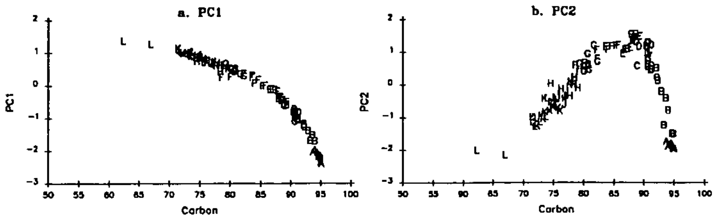

Figure - 3 Principal Components and Carbon

To explore the matter further, the correlations between the original variables and PCs were worked out (Table-3). PC1 is well correlated with all the variables. PC2 however correlates well only with Cvd, Hd, Od, F/V and to some extent with C/H. Significantly, PC3 and the rest show poor correlation with the variables, justifying PCA

Table - 3 Correlation matrix between variables and PCs

	PC 8	PC 7	PC 6	PC 5	PC 4	PC 3	PC 2	PC 1
CV	0.00	0.01	−0.04	0.12	−0.03	−0.11	0.65	−0.74
Fd	0.01	−0.01	−0.09	−0.05	−0.10	0.19	0.01	−0.97
Cd	−0.02	0.07	0.03	−0.07	−0.04	−0.03	0.29	−0.95
Hd	0.02	0.02	−0.05	−0.07	0.11	−0.14	0.50	0.84
Od	0.00	0.06	−0.06	0.06	0.02	0.07	−0.46	0.88
F/V	−0.02	−0.01	−0.06	−0.02	0.07	−0.25	−0.51	−0.82
C/H	0.04	0.02	0.04	0.02	−0.03	−0.10	−0.43	−0.89
CH/O	0.00	0.00	0.01	0.02	0.25	0.17	0.05	−0.95

After a few trials, it was realised that there was a good correlation between PC2 and Hd-Od/8 (HO/8) as well, which appears in the Dulong formula and which can be taken as a measure of the free hydrogen in coal. So, taking HO/8 as an additional variable, step-wise regression analysis between the PCs and the rest of the variables including HO/8 were carried out. The summarised results are presented in Table-4.

Table-4 Step-wise regression analysis

PC1		PC2	
Variable	Multiple Correlation	Variable	Multiple Correlation
Fd	0.971	HO/8	0.956
F/V	0.982	Cvd	0.967
Cd	0.997	F/V	0.999

Function1 = 0.1560 x Fd + 0.1511 x Cd + 0.1317 x F/V

Function2 = 0. 2050 x HO/8 + 0.4603 x Cvd - 0.3621 x F/V

PCs were plotted against the functions which are made up from a combination of the variables appearing in step-wise regression (Figure- 4 a & b).

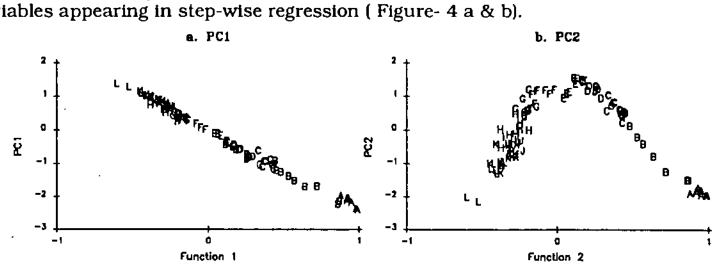

Figure - 4. Principal Components - Correlations

PC1 correlates very well with all the variables but seems to fit best with Fd and Cd. PC2 is highly influenced by HO/8. It is also related to Cvd and F/V to a lesser extent. PC2 vs Function2 resembles the graph PC1 vs PC2. It can be inferred that PC1 and PC2 probably represent Fd/Cd and the available hydrogen. Stated in a different way, it can be inferred that they represent the char and the volatile matter in coal. To probe further into this matter, Seyler's graph was plotted for the original data (Figure-5a) and a modified Seyler's graph was drawn using **Hd-Od/8** (HO/8) instead of Hd (Figure-5b). The shape of the graphs obtained clearly demonstrate that this is the **missing link between the original Seyler graph and the PC graph.** This brings the PCA to an end.

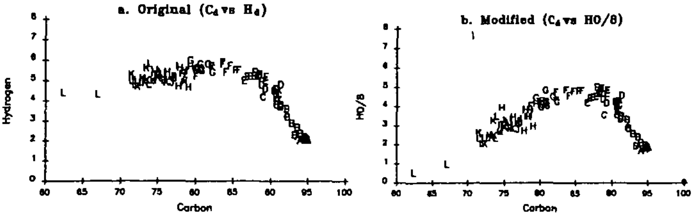

Figure - 5. Seyler Graph - ASTM Coals

3. PCA FOR INDIAN COALS

Twenty major Indian coal fields, based on their reserves were chosen and a statistical sample consisting of nearly 400 records was chosen from the publications of Central Fuel Research Institute's publications (CFRI,1978). The mean properties alone are given in Table-5 for each of these fields.

Table-5 Indian Coals - mean values

Field	Symbol	Cvd	Fd	Cd	Hd	Nd	Sd	Od	F/V	C/H	CH/O	Reserve Million Tons	% to Total
Bisrampur	○	7913	65.7	82.9	4.7	1.6	0.5	10.2	1.9	17.6	9.1	520	0.3
Bokaro	+	8565	70.4	88.2	5.0	2.0	0.6	4.5	2.4	17.7	19.3	9701	5.5
Godavari	⊠	7879	62.0	81.8	4.9	1.7	0.4	11.2	1.7	16.7	7.8	10771	6.1
Ib-River	⊕	7936	62.5	82.8	4.8	1.6	0.5	10.3	1.7	17.2	8.6	20757	11.7
Jharia	▽	8723	74.2	90.1	4.8	2.1	0.6	3.1	3.0	18.7	20.8	19417	11.0
Kamptee	△	7547	62.6	79.9	4.6	1.6	0.3	13.6	1.7	17.4	6.3	1372	0.8
Korba	⧗	7884	63.7	82.8	4.8	1.6	0.5	10.2	1.8	17.4	8.8	8021	4.5
N. Karanpura	∇	8049	63.8	84.1	5.0	1.9	0.7	8.1	1.8	16.8	11.7	13578	7.7
Pench-Kanyan	✖	8437	63.6	86.0	5.3	1.9	0.5	6.4	1.7	16.1	14.9	1955	1.1
Rajmahal	□	7520	58.9	78.9	4.8	1.7	0.6	13.9	1.4	16.6	5.3	10404	5.9
Ramgarh	⬠	8326	63.0	85.2	5.3	1.9	0.6	7.0	1.7	16.2	11.7	970	0.5
Raniganj	Y	8090	58.8	82.1	5.4	2.1	0.4	9.8	1.4	15.2	8.6	27245	15.4
Singarauli	¥	7606	60.6	79.8	4.9	1.6	0.6	13.2	1.5	16.4	6.3	9207	5.2
Sohagpur	⧅	8181	65.2	84.4	5.0	1.8	0.5	8.3	1.9	16.9	11.0	2145	1.2
S. Karanpura	⊠	7932	62.4	82.5	5.0	2.1	0.6	9.7	1.7	16.3	8.4	5148	2.9
Talcher	✳	7831	57.7	80.8	5.3	1.7	0.5	11.7	1.4	15.4	7.3	23547	13.3
Wardha	×	7493	59.5	78.7	4.7	1.7	0.4	14.4	1.5	16.6	5.9	4212	2.4
Others	♆	7772	63.5	81.8	4.7	1.7	0.5	11.3	1.8	17.3	7.9	3700	2.1
Tertiary coals	☆	8226	65.9	83.7	5.3	1.3	1.9	8.2	2.9	16.1	15.5	862	0.5
Neyveli lignite	◇	6673	44.1	71.4	5.2	1.1	1.8	22.6	0.8	13.5	3.6	3300	1.9

A similar procedure(normalisation, calculation of correlation matrix, eigen values and eigen vectors) was carried out on the Indian coals. The first two eigen values accounted for more than 90% of the variance (after removal of Sd and Nd). The analysis was carried out on an air-dried basis as well as on a dmmf basis on the 390 random values as well as the 20 mean values. PCs for the Mean values alone are plotted in Figure-6.

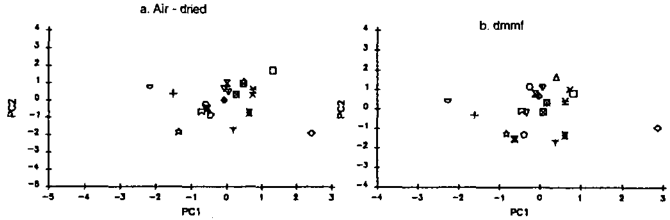

Figure - 6. Principal Components - Indian Coals - Mean Values

Jharia and Bokaro coals and the lignites stood out in both the cases. Rajmahal and tertiary coals looked different on air dried basis but came closer to the other coals on a dmmf basis. It means that their ash and moisture contents are significantly different from the rest. The rest of the samples, in both cases, fell into one small patch. A finer grouping has been done using cluster analysis but that is outside the scope of the present paper. The rest of the analysis and the results were similar to that of the US coals.

4. COMPARISON OF US AND INDIAN COALS

The Indian and US coals were analysed together next. It is worth stressing again that the US data covers almost all the (ASTM designated) ranks and hence serves as a good background. Comparisons are done at two levels- 119 US samples against the 390 Indian random samples at one level and the 12 US (rank-wise) mean values against the 20 Indian (field-wise) mean values at the other level. The same procedure was adopted and the PC graphs are shown in Figure-7. The graphs are exactly similar to Figure -1a and 1b.

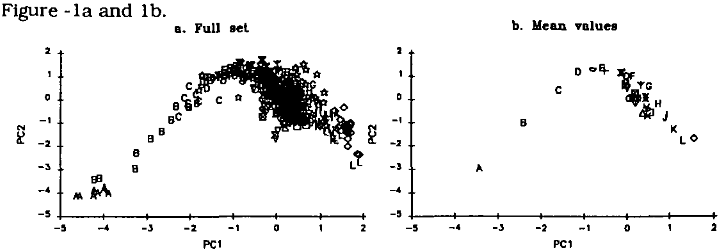

Figure - 7. Principal Components - US and Indian Coals

The 390 Indian samples fall into a small black patch in Figure-7a. A few lignite samples and Tertiary coal samples alone are visible in this graph. In Figure-7b, the Indian lignites fall with the US lignites. Bokaro and Jharia coals have the highest rank among Indian coals. Indian coals fall below the main line for the lower ranks.

The original and modified Seyler graphs were plotted for the 32 mean values (Figure - 8a and 8b). The Indian fields lie below the main graph which dips to the left. The higher oxygen content of Indian coals leads to a corresponding reduction in carbon and hydrogen contents.

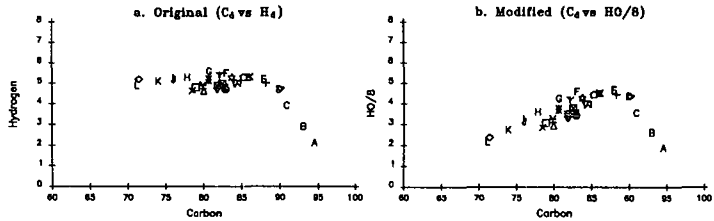

Figure - 8. Seyler Graph - US and Indian Coals - Mean Values

6. CONCLUSIONS

A graph of the principal components can be the new Seyler's graph for coal classification. The PCs seem to represent the rank. The graph shows a peak for the middle ranks. PC1 correlates best with Cd (and Fd) and PC2 with 'Hd- Od/8' (and Vd). PC1 and PC2 seem to represent the carbon and the available hydrogen in coal or broadly, the char and the volatiles of the coal. Among Indian coals, Jharia, Bokaro / Rajmahal/ Tertiary coals/Lignites look different and the rest show little variation. Cluster analysis can reveal a finer distinction.

The PCs are pseudo variables and not physical quantities. The choice of the variables is critical. The graphs at this stage can be used for comparative analyses. The stress is on methodology and the analysis can be repeated for other combinations of variables. There is a good potential for further research.

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INFLUENCE OF MACERAL COMPOSITION IN THE COMBUSTIBILITY OF SOME COLOMBIAN COALS.

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Keywords: Combustion, Macerals concentrate, TGA, buning profile.

The increase of international coal market has created new power operational problems and the need to reduce the carbon levels in ash below around 6% in order to render the pulverized fuel ash saleable as well as mantain the combustion efficieny (1).

Compared with the Northern hemisphere coals, many Gondwana coals contain high levels of maceral of the inertinite group. The inertinite maceral group is commonly regarde as the main source of unfused chars (2) and this can increase problems with carbon carryy-over in the fly ash, leading to less overall efficience and cost are incurred in its disposal.

Since coal is a very heterogeneous material consisting of different organic substances (macerals) and mineral matter to know the behavior of the different macerals in the combustion is important. The propose of the present work was to investigate the influence of maceral association in the burning profile of coal.

EXPERIMENTAL

Three samples of coal were crushed and analized by conventional ASTM method. The elemental analysis were carried out using Leco CHN-600 equipment and sulfur determinator Leco SC-132 equipment.

The demineralization of the coals were done by HF/HCl digestion as described by Radovic et al, (3). The demineralized sample were separated into different fractions using density gradient separation. The coal was placed in a vessel filled with density-gradient aquous CsCl ranging from 1.0-1.6 g/ml at 25°C. The density gradient method was developed using a glass colum of 1.5cm of id by 50 cm long. as show in the Figure 1. The solution was added into the column handly with care to avoid mixture. The order of addition was first the solution with the higher density in the sequence shown in the Figure 1.

Sample of 0.1-0.3 g of the demineralized coal was mixed with 0.5ml of Brij-35, a non ionic surfactant, as described by Dyrakacz and co-workers (4). The mixed sampled is fixed at the top of the colum with care and left for 90 minutes to permit the diffusion of the coal macerals according to their specific density. After the maceral separation the samples were filtered and the solution density was measured by refractometry index. Finally the coal sample were washed with destillated water and the maceral concentration was essesed using a microscop Leitz MPV-SP.

The combustiblity profile of the coals and macerals concentrated were done according to the method described in previous work (5). About 5mg of pulverized sample, less than 75μm was spread into the crucible and the system was heated at a heating rate of 20 °C min^{-1} until 900 °C. A residence time at 120 °C for 5 minutes was fixed to permit the release of moisture.Three points can be clearly define; the initial temperature (IT) is defined as the temperature at which the rate of weigt loss excess 0.1% after the moisture peak., the peak temperature (TP) is defined as the temperature at which the rate of weight loss was a maximun and the burnout temperature (BP) is the temperature at which the rate loss decreased less than 1.0% min^{-1}.

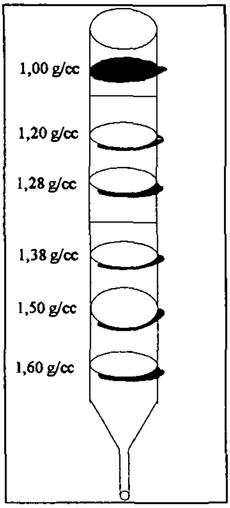

Figure 1: Sequence and density of the solution used.

RESULTS AND DISCUSSION

The analytical data of the coal used is presented in table 1. The samples belong to

Table 1. Analytical date of the coal used

Sample	H_2O	Ash a)	V.M (a)	%C (b)	%H (b)	%S (b)	%V (a)	%E	%I	R_o
GB-093	3.07	11.98	39.80	82.28	5.88	1.81	58.7	21.0	18.3	0.64
GB-148	3.24	18.50	37.21	82.46	6.97	1.59	61.1	18.3	8.2	0.68
Cerrejon	8.30	1.51	41.38	81.40	6.01	0.87	78.6	6.8	11.7	0.60

Where:(a), as determined; (b), moisture ash free basis, V, vitrinite, E, exinite, I, inertinite; R_o, reflectance.

bituminous coals.The density of the solution can be estimated by the refractive index, the straight line equation that relates density (X) with the refractive index (Y) was $Y=0.079747X + 1.2384$ with a correlation factor of 0.9996 The exinite was concentrate in the lower density solution while the inertinite concentrate in the higher density solution, Table 2. For all the samples vitrinite was the easier maceral to concentrate and in Cerrejon the vitrinite concentrated was +99%. Exinite and inertinite were difficult to separate indicating that the agregate of this macerals are presented in very fine particle.

The combustibility as measured by the burning profile method and using the IT index (6) shows (Table 3) that the mineral matter content has a negative effect upon combustion for the first two samples but in Cerrejón sample the mineral matter present a positive influence indicating that the mineral matter in this coal acts as catalyst during the combustion process.

Table 2: Maceral concentration in the dfferent density gradient .

Sample No	Density	Maceral concentration			
		%V	%E	%I	%MM
DGB-093	1.19	44.0	**48.0**	7.5	0.5
	1.27	**88.0**	8.0	4.0	--
	1.33	47.8	2.1	**49.5**	0.6
DGB-148	1.13	74.5	**23.5**	1.5	0.5
	1.26	**95.8**	2.1	1.6	0.5
	1.31	78.5	0.9	**20.0**	0.6
Dcerrejon	1.16	54.0	**39.0**	6.9	0.1
	1.23	**99.4**	0.3	0.2	0.1
	1.36	50.6	1.0	**48.2**	0.2

Where: D, demineriliized; % in volumetric; V, vitrinite; E, exinite
I, Inertinite.

Table 3 shows that exinite is the maceral easer to burn as shown by the burning profile peak index. The inertinite peacks shows that the burnout temperature is allways higher that the other two macerals and in the IT is also at higher temperature. According to this results the order for the combustibility facility of the macerals is: exinite>vitrinite>inertinite. The relative high concentration of inertinite in the Cerrejon coal may explain the operational problems that have been presented when using this coal directly in the utility it also conclude that some mineral matter is needed in this coal for better combustion.

Table 3. Combustion profile peaks of the origi l coals, demineriliized coals and their maceral concentrates.

Sample	IT	PT	BT
GB-093	293.6	673.4	787.6
DGB-093	261.5	619.3	782.1
GB-148	311.1	685.1	815.0
DBG-148	275.7	629.9	821.1
Cerrejon	306.0	591.4	758.8
Dcerrejon	334.5	620.6	819.5
Exinite concentrate GB-093	221.5	578.2	737.1
Vitrinite conentrate GB-093	294.4	651.9	750.0
Inertinite concentrate GB'093	262.2	620.2	752.5
Exinite concentrate GB-148	217.0	571.2	671.4
Vitrinite conentrate GB-148	240.4	594.6	715.6
Inertinite concentrate GB-148	255.8	610	766.0
Exinite concentrate Cerrejon	285.3	571.5	521.2
Vitrinite conentrate Cerrejon	293.3	579.5	738.7
Inertinite concentrate Cerrejon	317.8	603.8	791.1

Where: IT, Initial temperature; PT, Peak temperature or temperature of maximun burning rate; BT, Burnout temperature; D, demineriliized coal.

It can be conclude that maceral composition has a great influence in the reactivity of coal. The order of reactivity found was exinite>vitirinite>inertinite. The contend of mineral matter has also a great influence in the combustibility parameters.

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CHLORINATED ORGANIC COMPOUNDS EVOLVED DURING THE COMBUSTION OF BLENDS OF REFUSE-DERIVED FUELS AND COALS

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Keywords: Thermal analysis, evolved gas analysis, refuse derived fuels

ABSTRACT

The objective of this study was to examine the possible formation of chlorinated organic compounds during the combustion of blends of refuse derived fuels (RDF) and coal under conditions similar to those of an atmospheric fluidized bed combustion (AFBC) system. A series of experiments were conducted using a TGA interfaced to FTIR and MS systems. Additional experiments using a tube furnace preheated to AFBC operating temperatures were also conducted. The combustion products were cryogenically trapped and analyzed with a GC/MS system. The chlorination of phenols and the condensation reactions of chlorophenols were investigated in this study. A possible mechanism for the formation of chlorinated organic compounds such as dibenzodioxins and dibenzofurans, by chlorination and condensation reactions involving phenols, was proposed.

INTRODUCTION

The amount of municipal solid waste (MSW) generated in the United States each year has risen to nearly 200 million tons. The amount of waste generated and the rapidly declining availability of landfill space has forced municipalities to evaluate alternative waste management technologies. Incineration of unprocessed MSW is an area of concern since polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been reported as products of MSW combustion.[1]

Lindbaurer and coworkers[2] reported that co-firing MSW with 60% coal drastically reduced PCDD/PCDF levels. Gullett and Raghunathan[3] found that sulfur hindered PCDD and PCDF formation even at a sulfur/chlorine ratio of 0.64. The mechanism thought to be responsible for the inhibition is as follows:

$$SO_2 + Cl_2 + H_2O \rightarrow SO_3 + 2HCl \qquad (1)$$

This mechanism, and several others that have been proposed, recognize the existence of molecular chlorine (and not HCl) as an important precursor to the formation of chlorinated hydrocarbons during combustion. Although the presence of molecular chlorine is thought to be a key starting material, the conclusive reports in the literature about the possible formation of PCDDs and PCDFs in combustion systems are often contradictory and confusing.[4]

In previous work TG/FTIR/MS studies of the organic compounds evolved during combustion of blends of coal and refuse derived fuels revealed the production of phenols, furans, and various other organic materials during the combustion of paper and other cellulosic materials blended with coals.[5,6] The production of molecular chlorine during the combustion of polyvinyl chloride was also observed. Phenol, furan, and molecular chlorine could provide the important precursors for the formation of PCDDs and PCDFs in combustion processes. TG/FTIR/MS studies done by Lu[5] showed that more hydrocarbons are evolved at a fast heating rate due to incomplete combustion. These studies indicated there is a greater likelihood for the formation of chlorinated organic compounds at the fast heating rates, due to the concurrent evolution of HCl (which may be converted to molecular chlorine) and hydrocarbons, especially aromatics. Thus, chlorinated organic compounds may be formed at high heating rates, whereas products such as organic acids and alcohols are generally observed at slower heating rates.

A mechanism being proposed for the formation of chlorinated organics and possibly PCDDs and PCDFs is given in equations 2-4:

$$4HCl + O_2 \leftrightarrow 2H_2O + Cl_2 \text{ (Deacon reaction)} \quad (2)$$

$$C_6H_5OH + Cl_2 \rightarrow \text{chlorophenols} \quad (3)$$

$$\text{condensation of chlorophenols} \rightarrow \text{PCDDs and PCDFs} \quad (4)$$

This paper reports results from a series of studies designed to prove, or disprove, this proposed mechanism.

EXPERIMENTAL

Apparatus and Reagents - The TG/FTIR/MS system consisted of a TA Instruments SDT 2960 Simultaneous DTA-TGA system interfaced with a Perkin-Elmer 1650 Fourier Transform Infrared Spectrometer and a Fisons Instruments model VG Thermolab Mass Spectrometer. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for the GC/MS analysis. A twelve-inch Sola Basic Lindberg tube furnace was used for the preheated tube experiments. Reagents used include MC&B reagent grade phenol, EM Scientific HPLC grade dichloromethane, while 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol and dibenzofuran were 99+% grade from Aldrich.

To closely simulate conditions in an AFBC combustor, studies were conducted using a preheated quartz tube in the Lindberg tube furnace. The evolved gases were trapped in methylene chloride, concentrated, and analyzed using the GC/MS system. Combustion products of phenol and chlorophenols were also investigated. The detailed experimental conditions are outlined in the following paragraphs.

To examine the possibility of producing molecular chlorine via the Deacon reaction, as illustrated in equation 2, a mixture of air and 10% HCl in N_2 (air:HCl volume ratio of 2:1) was introduced into the quartz tube preheated to different temperatures in the tube furnace. The product gases were trapped in a phenol-methylene chloride solution and the solution analyzed for chlorophenols using the GC/MS system.

To examine the gas phase chlorination of phenol, as illustrated in equation 3, 100 mg portions of phenol were placed in a heated tube and evaporated in the presence of a constant flow 0.5% Cl_2 in N_2. Chlorination took place in the gaseous phase and the products were trapped in an aqueous solution of $NaHSO_3$, extracted by CH_2Cl_2, and analyzed using the GC/MS system.

The combustion of chlorinated phenols, which may lead to the reaction illustrated in equation 4, was examined by heating 100 mg portions of 2,4-dichlorophenol in the presence of air in the tube furnace. The combustion products were adsorbed by CH_2Cl_2 and identified using the GC/MS system. The reaction was also studied in a series of experiments in which 10 mg portions of 2,4-dichlorophenol were heated in air at a rate of 10°C/min in the TGA and the evolved gases were monitored (on-line) using the FTIR and MS spectrometers.

RESULTS AND DISCUSSION

The production of molecular chlorine by heating HCl in air followed by the chlorination of phenol in solution is an indication that the Deacon reaction (equation 2) takes place in the heated tube. Figure 1 shows the GC/MS results from these experiments conducted at different temperatures. The chromatograms indicate that the higher temperatures favor an increase in the production of chlorophenols. This indicates the Deacon reaction is favored at higher temperatures, which is consistent with thermodynamic calculations that show the Deacon reaction is favored above 590°C.

The gas phase chlorination of phenol (equation 3) experiments produced 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, as identified by NIST library matches and GC retention times of the pure materials. The chlorination of phenol began at temperatures around 250°C. At higher temperatures, dibenzofuran was produced. At still higher temperatures near 600°C, naphthalene was produced.

To examine the possible condensation of chlorophenols during combustion reactions, as is illustrated by equation 4, the compound 2,4-dichlorophenol was heated in air inside the tube furnace. The combustion products were trapped in methylene chloride, concentrated, and analyzed by GC/MS. Figure 2 shows examples of chromatograms for the combustion products. The products are indicated to be mainly 2,4,6-trichlorophenol, tetrachlorodibenzofuran, and dichlorodibenzodioxin, as identified by NIST library searches. The TG/MS experiments indicated the products of combustion include CO_2 (m/z = 44), H_2O (m/z = 18), HCl (m/z = 36) and trichlorophenol (m/z = 196), as is illustrated by the mass spectra profiles shown in Figure 3. This profile also shows the formation of chlorinated hydrocarbons at relatively low temperatures, which begins around 200°C. The small amount of material used, the slow heating rate, and the 300 amu limitation of the TG/MS system made it impossible to observe any larger chlorinated hydrocarbon product in this particular experiment. FTIR analysis of the evolved gases confirmed the emission of CO_2, CO and H_2O, and HCl, as labeled on the three dimensional plot in Figure 4.

CONCLUSIONS

Based on the information presented in this paper summary statements that can be made include:

- The Deacon reaction for the production of molecular chorine is generally favored at temperatures over 600°C.
- The gas phase chlorination of phenol is generally favored at temperatures over 600°C.
- Tetrachlorodibenzofuran, dichlorodibenzodioxin, and other chlorinated organic compounds are formed during the combustion of 2,4-dichlorophenol.
- The proposed three-step mechanism appears to be a possible pathway for the production PCDDs and PCDFs in combustion processes.

ACKNOWLEDGMENTS

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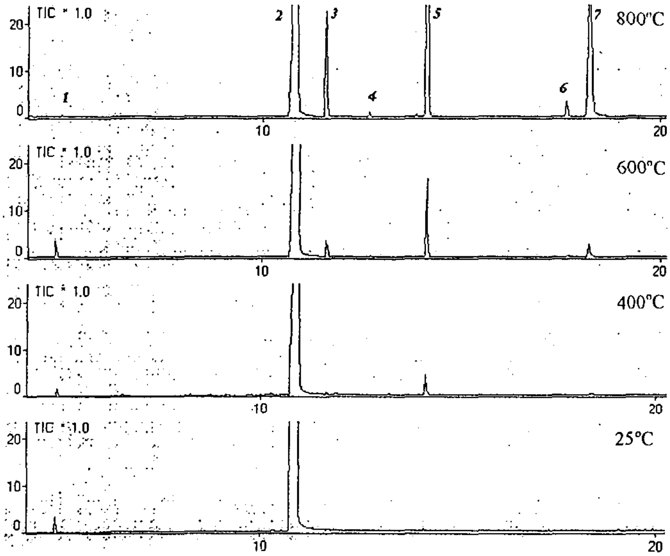

Figure 1. Chromatograms of the products from the reaction of HCl heated in air and trapped in a CH_2Cl_2 solution of phenol, concentrated, and analyzed by GC/MS. The MS assignments (NIST library matches) are as follows: 1 = cyclohexane, 2 = phenol, 3 = 2-chlorophenol, 4 = 2-chloro-cyclochlorocyclohexanol, 5 = *trans*-1,2-dichlorocyclohexene, 6 = 2,4-dichlorophenol, and 7 = 4-chlorophenol.

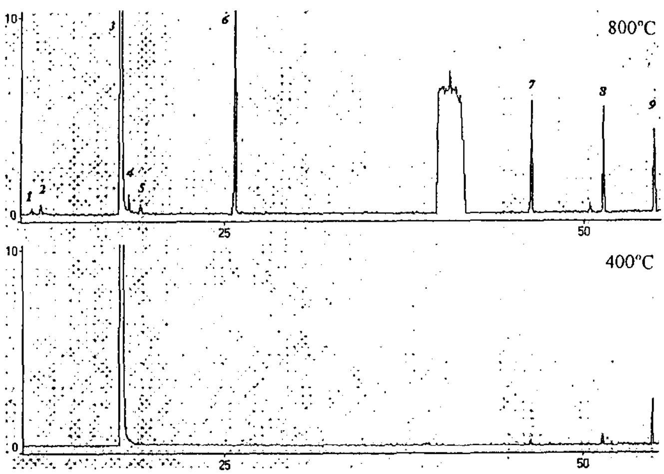

Figure 2. Chromatograms of the reaction products from the combustion of 2,4-dichlorophenol, which were trapped in CH_2Cl_2, concentrated, and analyzed by GC/MS. The MS assignments (NIST library matches) are as follows: 1 = 2-chlorophenol, 2 = dichlorobenzene, 3 = 2,4-dichloro-phenol, 4 = trichlorobenzene, 5 = 2,6-dichlorophenol, 6 = 2,4,6-trichlorophenol, 7 = dichloro-dibenzodioxin, 8 = trichlorodibenzodioxin, 9 = tetrachlorodibenzofuran.

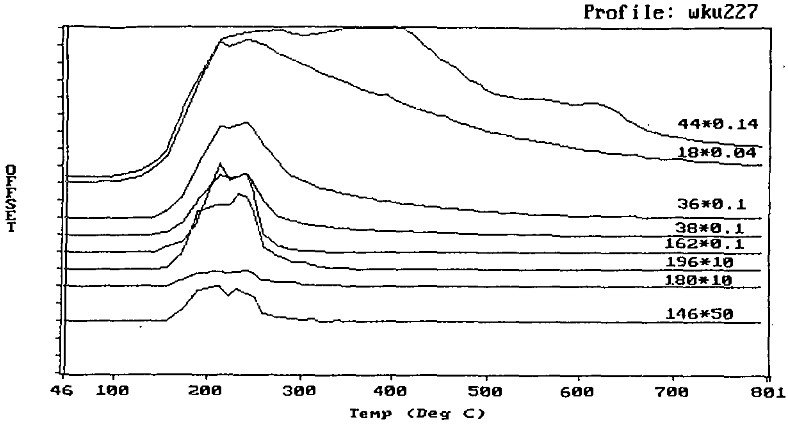

Figure 3. Mass spectra profiles for the combustion products of 2,4-dichlorophenol.

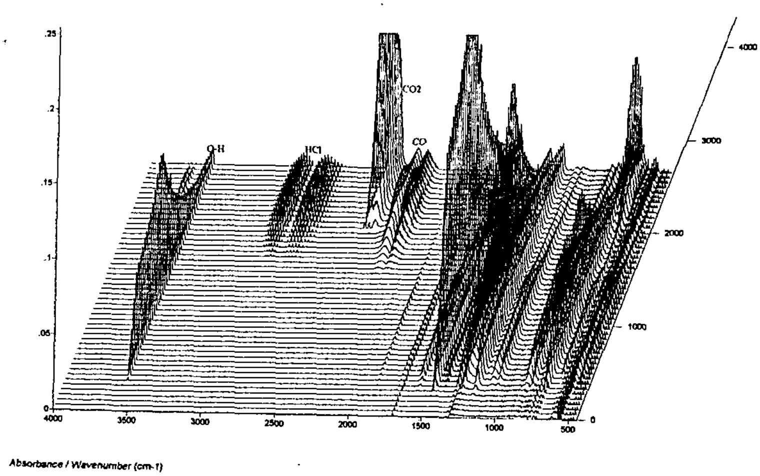

Figure 4. Three-dimensional FTIR spectra of the combustion products of 2,4-dichlorophenol.

COMBUSTION PROPERTIES OF COAL-CHAR BLENDS: NO_X EMISSION CHARACTERISTICS

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Key words: Combustion, NO_x Reduction, Coal-Char Blend

INTRODUCTION

Nitric oxide formation in hydrocarbon flames occurs primarily through three mechanisms; thermal NO (the fixation of molecular nitrogen by oxygen atoms produced at high temperatures), fuel NO (the oxidation of nitrogen contained in the fuel during combustion), and prompt NO (the attack of a hydrocarbon radical on molecular nitrogen). Of these three mechanisms, fuel NO is by far the most significant source of NO in practical coal flames [1].

It has been suggested that NO_X produced early in pulverized coal flames is subsequently reduced to N_2 by char/NO_X interactions [1]. NO_X can be both produced and reduced by heterogeneous char reactions. For some cases, as much as half of the fuel nitrogen remains in the coal after devolatilization [2]. The amount retained apparently is a function of the reactor stoichiometry [3]. Heterogeneous NO_X often accounts for 20-30 percent of the total NO_X formed [4, 5, 6]. The exact amount appears to be dependent on the temperature and extent of devolatilization. The rate of heterogeneous NO_X reduction has been investigated by many researchers [1, 7, 8, 9]. Essentially, char reduction of NO_X begins only after oxygen is locally depleted in the reactor [10]. The heterogeneous destruction reactions have been determined to be significant in fuel-lean conditions for char combustion, but for fuel-rich coal combustion, the reduction reactions in the gaseous phase appears to control reaction rate [11]. CO enhances NO_X reduction due to surface catalysis of the NO/CO reaction [1, 7]. In the absence of CO, the char-NO_X reduction rate is controlled by the dual-site mechanism of absorbed NO_X [12]. In the presence of CO, the controlling step is the reaction of gaseous NO_X and absorbed NO_X at an active site to form N_2, CO_2, and an oxide complex. Water and O_2 were reported to inhibit the reaction due to the buildup of a chemisorbed layer of oxygen on the char surface [1,12].

The primary goal of this study was to investigate the concept of lowering NO_X emissions by co-firing pulverized Illinois coal with char in a practical flame. A summary of the results obtained is presented in this paper.

EXPERIMENTAL

Coal-Char Blends - A continuous feed charring reactor was used for producing char samples from an Illinois No. 6 coal (38% volatile matter, dry basis). Char samples were pulverized to 70% minus 200 mesh. Pulverized coal (70% minus 200 mesh) was mixed with either the char or powder activated carbon (Calgon Carbon Company) to prepare the following blends:

Blend 1: 125 pounds of 12.5% char - 87.5% coal
Blend 2: 500 pounds of 25% char - 75% coal
Blend 3: 125 pounds of 50% char - 50% coal
Blend 4: 125 pounds of 12.5% activated carbon-87.5% coal

Proximate and ultimate analyses of the fuels and pore area and pore volume of the coal, char, and activated carbon were determined.

Combustion Tests - Combustion tests were performed with the coal and blends in a 0.5-1.0 Mbtu/hr combustor located at Brigham Young University (BYU) Advanced Combustion Engineering Research Center (ACERC). The combustor, referred to as a controlled profile reactor (CPR), is a cylindrical, down-fired reactor with an inside diameter of 0.80 m and a length of 2.40 m [13]. The burner consists of a central fuel injection tube surrounded by a swirling annular jet of secondary air. The secondary air is preheated to about 500 F and passes through a moveable-block swirl generator capable of varying secondary swirl number from 0 to 5.

Thirteen combustion tests were performed. The first three test were to establish base combustion conditions of the coal only, with no char addition. Tests 4 and 5 were performed to investigate the in situ capture of SO_2 by a high surface area hydrated lime. The remaining tests were designed to determine the ability to reduce NO_X by the coal-char blends. In all combustion tests, effluent gas and solid samples were collected and analyzed.

RESULTS AND DISCUSSION

Properties of Coal-Char Blends- Table 1 compares the proximate analyses of the coal, char (mixture of all char samples ground to -200 mesh), and the blends. The volatile matter (VM) and H-T ash contents of the char were 16.2 and 16.7 wt% (dry basis) compared to 38 and 12.4 wt% for the coal. The VM contents of the blends ranged from 27.3 wt% for the coal-activated carbon blend to 35.6 wt% for the 12.5% char - 87.5% coal blend. As summarized in Table 2, sulfur and nitrogen contents and Btu/lb values of the coal and blends were comparable (3.17 to 3.41% S; 1.20 to 1.33% N; and 12,047 to 12,182 Btu/lb).

The nitrogen-BET pore area of the char was 15.7 m^2/g compared to 1012 m^2/g for the powder activated carbon, Table 3. The pore area of the coal was 18.8 m^2/g indicating that during charring some of the macropores were blocked or destroyed. Nevertheless, char should have micropore area of about 100-400 m^2/g. Micropore area is measured by CO_2 adsorption which was not performed in this study.

Combustibility of Coal-Char Blends- The combustion test matrix is shown in Table 4. Flame temperatures were recorded for the base test condition noted as test 1 and for tests 8-10, 12 and 13. An axial temperature profile was made during test 1. Peak centerline flame temperature was recorded at the 28 cm axial location. Therefore, subsequent characteristic centerline flame temperatures were measured during tests 8-10 and 12, 13 at the 28 cm axial location. The flame temperature measurements are shown in Figure 1.

The effect of char addition to the coal on carbon burnout is shown graphically in Figure 2. Carbon burnout increased with initial increase in percent char in the fuel and decreased slightly with additional char. Visually the flame was stable but became more detached from the burner and flickered at the highest char percentage. Volatile content of the fuel is important to flame stability and therefore burnout. By increasing the char content, the volatile content is decreased resulting in greater flame instability.

Figure 3 shows the measured increase in effluent NO_x concentrations with increasing combustion temperature for the combustion tests performed for this study. Effluent NO_x concentrations in combustion systems is known to increase with combustion temperature [14, 15] due mainly to the increase in thermal NO_x production.

Figure 4 shows the effect that increasing stoichiometry has on effluent NO_x values. Since conversion of fuel nitrogen to NO depends on the availability of oxygen atoms, an increase in effluent NO_x values with increasing stoichiometric ratio was expected. The reason for the stronger dependance noticed for the 0% compared with the 25% char case deserves further investigation.

In order to determine the effect of NO_x reduction on char surfaces during combustion, other NO_x producing or reducing factors must be accounted for. For example, if NO_x is noticed to decrease with increasing char in the fuel, is the effect due to the addition of more NO_x reduction sites on the char surfaces, or from the decrease in burnout and therefore release of fuel nitrogen, or from the decrease in flame temperature and subsequent decrease in the production of thermal NO_x. In coal combustion, fuel nitrogen is certainly the dominant source of NO_x [16]. Since it has been shown that fuel nitrogen evolves from coal particles at approximately the same rate as carbon is consumed [16, 17], the fuel nitrogen release and therefore production of fuel NO_x can be corrected for burnout. Thermal NO_x contributions can be subtracted from total NO_x if the temperature dependence is known. Previous natural gas combustion tests performed using the CPR provided thermal NO_x concentrations as a function of flame temperature [8]. This correlation indicates that only about 10% of the effluent NO_x values measured during these combustion tests originated as thermal NO_x.

Figure 5 shows the effect of increasing percentage of char in the fuel on effluent NO_x concentrations. In order to reduce other NO_x producing and reducing effects as much as possible, these NO_x values have been corrected for burnout as well as thermal NO_x. The trends show a slight initial increase in NO_x with addition of char in the fuel but subsequently NO_x decreases with additional char.

NO_x levels are shown to increase with addition of small amounts of char to the fuel stream. However, an almost linear reduction in NO_x values is noted with increasing char above 12.5%. The reason for the initial increase in NO_x values is not well understood. It is likely that the addition of char extends the reaction zone allowing for greater mixing of fuel and combustion air so that a greater percentage of fuel nitrogen is released in a more oxygen rich environment causing amine radicals to oxidize to NO rather than molecular nitrogen. This explanation is substantiated by the observation that the 12.5% activated carbon-coal blend produced slightly higher effluent NO_x levels than the 12.5% char-coal blend. The low volatile content of activated carbon, and hence, low reactivity, would cause it to lengthen the reaction zone to a greater extent than the addition of 15% volatile content char.

Establishing additional carbon sites by blending char with the coal in the feed stream, along with increasing the NO-carbon contact time, may enhance the effectiveness of the NO reactions. This may account for the measured decrease in NO with additional char. Additional near burner testing or modeling of the combustion system may provide insight into this phenomenon.

SUMMARY AND RECOMMENDATIONS

Blending char with parent coal may have some merit as a viable NO_x reduction scheme for high values of char addition (ie, above 40%). It is recommended that future work be aimed at using high surface area char and increasing the stability of high char content fuels by studying the effect of parameters such as air preheat, burner geometry, and gas or oil assist. The effect of different types of char and injection location (temperature) on the effluent NO_x concentration should also be investigated.

The increase in effluent NO_x concentration with low levels of char blended with coal is not well understood. It is recommended that fuel nitrogen partitioning studies be performed to determine the separate relationships between volatile and char nitrogen on effluent NO_x. It is also recommended that near burner combustion tests be performed to study the fate of NO_x precursors in coal and coal-char flames.

ACKNOWLEDGMENTS

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Table 1. Proximate analyses of fuels (wt %, dry basis)

	Coal	Blend 1	Blend 2	Blend 3	Blend 4	Char
moisture	12.5	10.4	8.8	6.4	11.7	2.11
volatile matter	38.0	35.6	32.9	27.3	34.7	16.2
fixed carbon	49.6	51.3	53.7	58.3	54.2	67.1
H-T *ash*	12.4	13.2	13.4	14.4	11.1	16.7

* minus 200 mesh samples

Table 2. Analysis of fuels (wt%, dry basis)

	Coal	Char	Blend 1	Blend 2	Blend 3	Blend 4
Nitrogen	1.33	1.46	1.30	1.34	1.42	1.29
Sulfur	3.41	2.83	3.31	3.27	3.09	3.17
Btu/lb	12,182		12,138	12,169	12,047	12,480

Table 3. Pore area and pore volume data

	Coal	Char	Activated Carbon
Pore area (m^2/g)	18.8	15.71	1012
Pore volume (cc/g)	0.0342	0.145	

Table 4. Combustion Test Matrix.

Test No.	Description	Fuel Feed Rate (kg/hr)	Air Feed Rate (kg/hr)	Stoichiometric Ratio[1]
1	Coal	11.4	96.4	1.08
2	Coal	11.4	110.0	1.24
3	Coal	11.4	93.5	1.05
4	Hydrated Lime Injection	11.4	96.4	1.08
5	Activated Carbon Injection	11.4	96.4	1.08
6	Coal - 25% Char	11.4	100.9	1.09
7	Coal - 25% Char	11.4	93.5	1.01
8	Coal - 25% Char	11.4	114.5	1.23
9	Coal - 25% Char	18.2	160.1	1.08
10	Coal - 25% Char	11.4	79.4	0.85
11	Coal - 12.5% Char	11.4	100.9	1.08
12	Coal - 12.5% Activated Carbon	11.4	102.0	1.09
13	Coal - 50% Char	11.4	103.2	1.08

[1] Stoichiometric ratio is actual A/F divided by stoichiometric A/F.

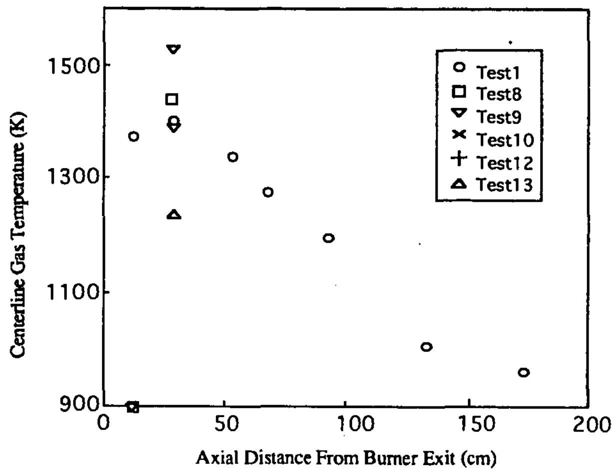

Figure 1. Gas temperature measurements for selected CPR combustion tests.

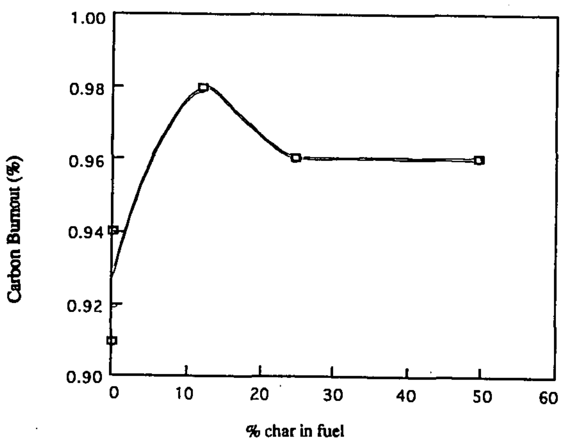

Figure 2. Effect of char concentration in the fuel on carbon burnout.

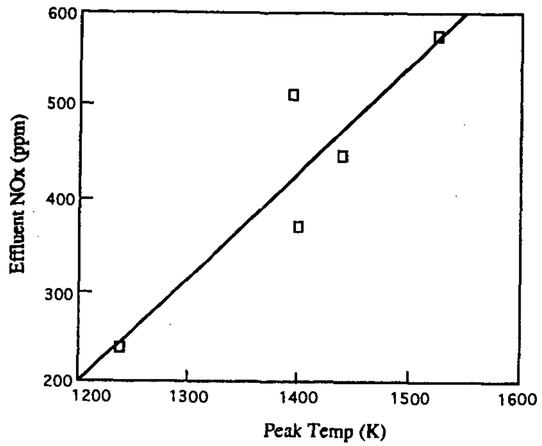

Figure 3. Relationship of peak flame temperature with measured effluent Nox concentration.

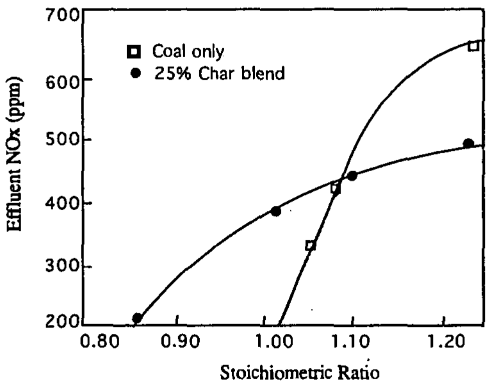

Figure 4. Effect of stoichiometric ratio on effluent Nox (Fuel feed 11.4 kg/hr).

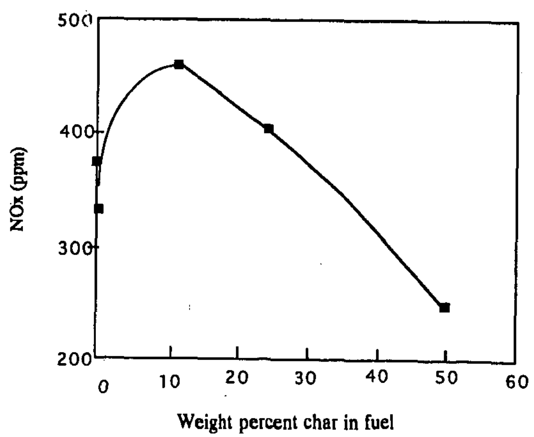

Figure 5. Effect of char concentration on effluent Nox emissions (corrected for burnout and thermal Nox; fuel feed 11.4 kg/hr, SR = 1.08).